

## AN INVESTIGATION OF THE EFFECT OF COAL PRETREATMENT ON LIQUEFACTION BEHAVIOR

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The effect of coal pretreatment on thermal and catalytic liquefaction behavior was examined in this study. Black Thunder coal, a subbituminous coal from Wyoming, was used untreated and after pretreatment with SO<sub>2</sub>. SO<sub>2</sub> pretreatment involved crushing and sizing the coal and then contacting the coarse fraction with aqueous SO<sub>2</sub> to remove alkali and alkaline metals. This treatment was followed by a gravity separation to recover the fraction with the lowest ash content.<sup>1</sup> Analysis of these coals presented in Table 1 indicates that the SO<sub>2</sub> treatment of Black Thunder coal doubles the amount of sulfur in the coal but halves the amount of ash present.

In this study, the effect of different slurry-phase catalyst precursors, most of which were oil-soluble, on the liquefaction behavior of both the untreated and SO<sub>2</sub> pretreated coal was examined. The first set of experiments was performed without a solvent but with the addition of a probe hydrogenation species, pyrene. The second set of experiments was performed with selected catalysts and pyrene but with using a solvent in the liquefaction reactions. The solvents chosen were a non-donor solvent, 1-methylnaphthalene, a coal-derived solvent, V1074, and a hydrogen donor solvent, 9,10-dihydroanthracene. The last set of experiments evaluated the combination of two types of coal pretreatment, in which the untreated and SO<sub>2</sub> treated Black Thunder coals were preswelled prior to liquefaction reactions. The swelling solvents chosen were methanol, isopropanol, tetrahydrofuran and dimethylsulfoxide on the basis of the research performed at Amoco in conjunction with this work.<sup>2</sup> The liquefaction reactions were performed thermally and catalytically. Ni octoate was chosen as the catalyst because of its demonstrated activity while 1-methylnaphthalene was chosen as the reaction solvent because of its apparent noninteraction with the coal and pyrene system which would allow the effect of preswelling as a pretreatment method to be clearly demonstrated.

### EXPERIMENTAL

**Catalyst Screening Test.** The catalytic activity of a number of different catalysts for coal conversion of untreated and SO<sub>2</sub> treated Black Thunder coal and pyrene hydrogenation was evaluated with and without solvent. The system without solvent was composed of 1.5 g pyrene, 20 wt% coal and a nominal 600-700 ppm of active metal from the catalyst precursor based on the coal feed. The coals used were untreated Black Thunder coal and SO<sub>2</sub> treated Black Thunder coal which were obtained from Amoco. Proximate and ultimate analyses for both coals are given in Table 1. The catalyst precursors tested were molybdenum naphthenate (Shepherd Chemical), iron naphthenate (Aldrich), nickel naphthenate (Shepherd Chemical), nickel octoate (Shepherd Chemical), chromium 2-ethylhexanoate (Strem Chemical), and vanadium naphthenate (Strem Chemical). The reactions were performed using ~20 ml stainless steel tubular reactors at 410° for 30 min and were agitated horizontally at 450 cpm. The pyrene reaction products were analyzed by gas chromatography using a Varian Model 3400, a J&W DB column and flame ionization detection. Pyrene conversion and hydrogenation were used to compare the effect of the catalyst and coal pretreatment on the hydrogenation reactions. Pyrene hydrogenation is defined as the moles of hydrogen required to form the liquid hydrogenation products from pyrene as a percentage of the moles of hydrogen required

to form the most hydrogenated product, perhydropyrene. Coal conversion to THF solubles was also determined.

The reaction systems with solvent employed these different solvents: 9,10-dihydroanthracene, 1-methylnaphthalene, and V1074, a coal derived solvent from the Wilsonville Coal Liquefaction Research and Development facility. The coals used were untreated and SO<sub>2</sub> treated Black Thunder coals. The catalysts employed with the different solvents were nickel octoate, cobalt naphthenate and chromium naphthenate with 9,10-dihydroanthracene; nickel octoate with V1074; and nickel octoate and chromium naphthenate with 1-methylnaphthalene. The reaction conditions used were 410 °, 1250 psig H<sub>2</sub> at ambient temperature, 30 min reaction time, 1.33 g maf coal, 0.67 g pyrene, 2.00 g of solvent, and catalyst loading of 600 to 700 ppm of active metal based on coal feed. The reactors were the same as previously described. The pyrene reaction products and coal conversion were obtained as stated earlier.

**Coal Swelling Reactivity Test.** For the coal swelling reactivity test, four swelling solvents were used: methanol, isopropanol, tetrahydrofuran, and dimethylsulfoxide, all of which were obtained from Fisher Scientific and were used as received. Untreated and SO<sub>2</sub> treated Black Thunder coals were swelled prior to reaction by introducing 2 g of coal to a swelling tube along with 7 ml of swelling solvent. After 2 hr the amount of coal swelling that occurred was determined by measuring the height of the coal and comparing that to the height of the coal prior to swelling. The coal remained in the swelling solvent for a total of 24 hr, after which the solvent was removed from the coal and dried for 7 hr at room temperature; the weighed coal was placed in the liquefaction reactor and then reacted at 410° for 30 min under well-agitated conditions. Each reaction contained a nominal 1.33 g of maf coal, 2.00 g of 1-methylnaphthalene as solvent, 0.67 g of pyrene, and any residual swelling solvent remaining in the coal for those reactions performed with prior solvent swelling. Hydrogen gas was introduced at 1250 psig at ambient temperature. Reactions were performed thermally and catalytically; the catalyst used was nickel octoate introduced at a level of 600 to 800 ppm of active metal

## DISCUSSION OF RESULTS

**Effect of Catalyst Precursors on Coal and Pyrene Conversion.** Liquefaction reactions were performed with untreated and SO<sub>2</sub> treated Black Thunder coals without a solvent using pyrene as a probe hydrogenation species. The amount of coal conversion, pyrene conversion and pyrene hydrogenation (HYD) achieved with the different catalyst precursors is presented in Table 2. With each catalyst precursor when no solvent was present, the coal conversion was higher with the SO<sub>2</sub> treated coal than with the untreated. In the reactions with Mo naphthenate, the amount of coal conversion was almost doubled, while Fe naphthenate, Ni naphthenate, and Ni octoate showed substantial improvements with the SO<sub>2</sub> treated coal. The catalyst precursors that had the least effect on coal conversion for untreated Black Thunder coal were Mo naphthenate and Cr 2-ethylhexanoate which yielded average coal conversions of 48.1 and 48.0%, respectively.

Pyrene conversion varied considerably depending upon the type of catalyst precursor present and the amount of sulfur present in the system (Table 2). Pyrene conversion for the untreated coal system was greatest with Ni octoate and Ni naphthenate while Mo naphthenate, Fe naphthenate, Cr 2-ethylhexanoate and V naphthenate showed low activity. The presence of the additional sulfur in the SO<sub>2</sub> treated coal affected some of the activity for pyrene conversion for the different catalysts. Mo naphthenate increased substantially from 3.4% in the untreated system to 26.3% in the SO<sub>2</sub> treated system. Cr 2-ethylhexanoate doubled in pyrene conversion but still showed low activity. Ni octoate was active with the SO<sub>2</sub> treated coal just as it was with the untreated coal. The primary hydrogenation product from pyrene observed with all of the catalyst precursors was dihydropyrene

(DHP) while the more active catalysts also yielded tetrahydropyrene (THP) and hexahydropyrene (HHP) as the reaction products.

When solvents were used in the liquefaction reaction in the presence of catalyst precursors, interactions between the solvent and catalyst precursor became apparent. For example, Ni octoate was used with all three solvent systems; for both untreated and SO<sub>2</sub> treated Black Thunder coal, the hydrogen donor solvent, 9,10-dihydroanthracene (DHA), produced the highest coal conversion, followed by coal-derived V1074 with the nondonor, 1-methylnaphthalene (1-MN), yielding the least conversion. The reactions with Cr naphthenate in DHA yielded coal conversions of ~77 and ~79% for untreated and SO<sub>2</sub> treated coals while in 1-MN the conversions with Cr naphthenate were ~53 and ~52%, respectively. Pyrene conversions tended to vary rather substantially and appeared to be influenced by the specific interactions of the solvent with the catalyst and probe pyrene molecule. The highest conversions of pyrene were observed with Ni octoate in 1-MN, but nearly twice as much pyrene conversion was obtained with SO<sub>2</sub> treated coal than with untreated coal. The primary hydrogenation products from pyrene in the reactions with the solvents were DHP; only minor amounts of THP were formed when DHA was solvent while neither THP nor HHP was formed with the other two solvents.

**Effect of Solvent Preswelling on Liquefaction Reactions.** Four swelling solvents, THF, methanol, isopropanol, and DMSO, were employed to preswell untreated and SO<sub>2</sub> treated coals. The swelling of the SO<sub>2</sub> treated and untreated Black Thunder coals ranked as methanol = isopropanol < THF < DMSO. DMSO swelled the untreated coal by 100% so that the volume of the coal doubled. The other swelling solvents, methanol, isopropanol and THF, swelled the untreated coal by 16 to 42% with THF being the most effective among the three. Methanol and isopropanol remained in the coal in similar amounts which ranged from 0.9 to 1.3 g for 1.6 to 1.7 g of coal. THF showed more inclusion in the coal leaving between 1.45 to 1.7 g in 1.6 to 1.7 g of coal while DMSO left between 3.1 to 4.3 g in 1.62 g of untreated coal.

All of the swelling solvents increased the volume of the SO<sub>2</sub> treated coal more than they did for the untreated coal, although the swelling ranking was the same. Again DMSO remained strongly absorbed in the coal after removal of the swelling solvent with amounts ranging from 4.0 to 5.7 g. By contrast, nearly 2.0 g of THF and about 1.0 g of either methanol or isopropanol was retained in an equivalent amount of coal.

Liquefaction reactions were performed thermally without a catalyst and with Ni octoate. Ni octoate was chosen as the catalyst because of its demonstrated high activity for coal conversion. Table 3 presents the change in coal volume upon swelling, coal conversion and pyrene conversion for both untreated and SO<sub>2</sub> treated coals. The addition of Ni octoate increased the amount of coal conversion achieved regardless of swelling solvent or no swelling solvent. Likewise, pyrene conversion was increased with Ni octoate present in the reaction medium.

The preswelling solvent which showed the most improvement for coal conversion compared to no preswelling for thermal reactions of untreated coal was isopropanol and THF for the SO<sub>2</sub> treated coal. Methanol yielded the greatest improvement in the reactions with Ni octoate for both untreated and SO<sub>2</sub> treated coals. By contrast, DMSO, which was the most effective swelling solvent and had the highest incorporation into the coal, was most detrimental for coal conversion. The SO<sub>2</sub> pretreated coal reacted with Ni octoate was more adversely affected by DMSO than the untreated coal.

Pyrene conversion varied according to the reaction condition. For untreated Black Thunder coal systems, the highest pyrene conversion was achieved with Ni octoate with methanol and without preswelling solvent. For the SO<sub>2</sub> treated Black Thunder coal systems, the highest pyrene conversion was obtained with Ni octoate and no preswelling solvent followed by Ni octoate with DMSO as preswelling solvent. Product distributions achieved from pyrene with coal preswelling yielded DHP

as the primary product for reactions with Ni octoate and occasionally with the thermal reactions depending upon the type preswelling solvent. Some HHP was formed with the Ni octoate systems depending again upon the preswelling solvent.

### SUMMARY

SO<sub>2</sub> pretreatment of Black Thunder coal enhanced the liquefaction behavior of the coal in the presence of different catalytic agents regardless of whether a solvent was present or not. A hydrogen donor solvent, 9,10-dihydroanthracene, promoted increased coal conversion compared to nondonor and coal-derived solvents. Pyrene conversion and hydrogenation were highly dependent upon the catalyst type and upon the presence of sulfur in the system. For Mo naphthenate the sulfur in SO<sub>2</sub> treated Black Thunder coal with solvent present promoted pyrene conversion while for Ni octoate, the sulfur was detrimental to pyrene conversion. The presence of solvent in the liquefaction reaction tended to level the amount of pyrene conversion although 1-methylnaphthalene had a lesser effect than did the other two solvents.

Swelling coal prior to liquefaction reactions had a more positive effect with untreated Black Thunder coal than with the SO<sub>2</sub> treated as shown in Table 4. The only swelling solvent that was detrimental to coal conversion for the untreated coal was DMSO while for the SO<sub>2</sub> treated coal only methanol showed an improvement in coal conversion. Hence, coal preswelling was most effective for untreated Black Thunder coal.

### NOMENCLATURE

% HYD	=	percent hydrogenation	maf	=	moisture and ash free
1-MN	=	1-methylnaphthalene	PYR	=	pyrene
DHA	=	dihydroanthracene	THF	=	tetrahydrofuran
DHP	=	dihydropyrene	THP	=	tetrahydropyrene
HHP	=	hexahydropyrene			

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### REFERENCES

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Table 1. Proximate and Ultimate Analysis of Untreated and SO<sub>2</sub> Treated Black Thunder Coals<sup>a</sup>

	Proximate Analysis <sup>b</sup>		Ultimate Analysis <sup>c</sup>	
	Untreated	SO <sub>2</sub> Treated	Untreated	SO <sub>2</sub> Treated
% Moisture	11.2	9.9	% Carbon	69.7
% Ash	5.4	3.1	% Hydrogen	4.9
% Volatile Carbon	44.5	41.7	% Nitrogen	0.9
% Fixed Carbon	38.8	45.3	% Sulfur	0.4
Total	100.0	100.0	% Ash	6.1
Btu/lb	10606	10993	% Oxygen (by difference)	18.0
				19.4

<sup>a</sup>Commercial Testing and Engineering Co., Birmingham, AL

<sup>b</sup>As Received

<sup>c</sup>Dry Basis

**Table 2. Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO<sub>2</sub> Treated Black Thunder Coal With and Without Solvents\***

Catalyst	Untreated Black Thunder Coal			SO <sub>2</sub> Treated Black Thunder Coal		
	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD <sup>b</sup>	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD <sup>b</sup>
<b>No Solvent</b>						
None	59.6±0.9	1.6±0.1	1.0±0.1	57.5±11.5	1.3±0.4	0.8±0.3
Mo Naphthenate	48.1±1.8	3.4±1.7	1.1±0.6	85.7±2.1	26.3±2.5	9.2±0.9
Fe Naphthenate	54.2±11.2	1.4±0.1	1.0±0.3	63.4±2.8	4.9±4.2	2.1±1.6
Ni Naphthenate	62.7±10.9	13.1±6.8	5.7±1.5	73.9±5.7	15.8±0.4	5.7±0.1
Va Naphthenate	64.4	4.2	2.0	66.1±1.8	3.9±0.7	1.9±0.3
Ni Octoate	73.8±6.0	25.6±0.1	9.1±0.0	84.4±7.6	21.9±2.0	7.8±0.7
Cr 2-Ethylhexanoate	48.0±7.9	1.2±0.3	0.8±0.2	54.8±1.5	3.3±1.6	1.5±0.6
<b>Solvent: 1-Methylnaphthalene</b>						
None	49.3±0.8	3.5±1.1	2.1±0.6	47.3±1.1	1.5±1.1	0.7±0.7
Ni Octoate	70.7±4.1	6.8±0.3	2.3±0.1	76.3±4.2	12.5±3.5	4.2±1.2
Cr Naphthenate	52.7±1.8	0.0±0.0	0.0±0.0	51.7±1.1	0.0±0.0	0.0±0.0
<b>Solvent: V1074</b>						
Ni Octoate	81.5±0.9	6.8±4.3	2.4±1.6	82.1±3.0	2.0±2.8	0.7±0.9
<b>Solvent: 9,10-Dihydroanthracene</b>						
Ni Octoate	87.0±1.7	4.4±1.1	2.1±0.3	92.4±5.0	3.7±1.4	1.8±0.5
Co Naphthenate	83.2±0.1	2.1±0.2	1.3±0.1	85.9±0.8	2.7±0.4	1.6±0.3
Cr Naphthenate	76.8±4.2	4.0±0.0	2.6±0.0	78.6±5.7	2.9±1.3	2.0±0.9

\*Reaction Conditions: 410°C, 30 min, 1250 psig H<sub>2</sub> at ambient temperature, agitated at 450 rpm.

<sup>b</sup>HYD = hydrogenation

Table 3. Effect of Solvent Preswelling on Reactions of Untreated and SO<sub>2</sub> Treated Black Thunder Coal in 1-Methylnaphthalene<sup>a</sup>

Catalyst	Swelling Solvent	Untreated Black Thunder Coal			SO <sub>2</sub> Treated Black Thunder Coal		
		Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)	Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)
None	None	NA	49.3±0.8	3.5±1.1	NA	47.3±1.1	1.5±1.1
Ni Octoate	None	NA	70.7±4.1	6.8±0.3	NA	76.3±4.2	12.5±3.5
None	THF	34.2±7.0	59.7±8.9	0.0±0.0	87.6±2.7	58.0±9.5	0.0±0.0
Ni Octoate	THF	41.3±0.6	77.0±0.1	2.4±0.1	97.4±3.7	72.5±5.8	2.2±0.4
None	Methanol	26.7±0.8	53.9±2.8	1.0±0.3	38.4±2.3	41.8±2.4	1.5±0.1
Ni Octoate	Methanol	18.6±0.6	85.5±0.1	10.9±0.4	31.6±7.4	78.6±1.1	4.9±0.8
None	Isopropanol	16.9±5.5	61.7±1.1	0.8±1.1	45.0±0.0	56.4±3.0	1.6±0.1
Ni Octoate	Isopropanol	16.3±3.8	77.6±1.1	2.2±0.4	32.3±6.4	73.9±5.1	3.9±0.6
None	DMSO	111.7±3.7	29.3±4.0	1.2±0.5	176.5±26.2	29.8±3.2	1.3±0.4
Ni Octoate	DMSO	102.4±9.5	63.6±3.6	5.0±0.8	171.6±11.9	50.1±9.5	7.1±1.1

<sup>a</sup> Reaction Conditions: 410°, 30 min, 1250 psig at ambient temperature agitated at 450 cpm.

Table 4. Comparison of the Effect of Swelling Solvents on the Liquefaction of Untreated and SO<sub>2</sub> Treated Black Thunder Coal

Swelling Solvents	Untreated Black Thunder Coal Percent Change in				SO <sub>2</sub> Treated Black Thunder Coal Percent Change in					
	Coal Conversion		Pyrene Conversion		Swelling Index (ΔV%)	Coal Conversion		Pyrene Conversion		Swelling Index ΔV %
	Thermal	Ni Octoate	Thermal	Ni Octoate		Thermal	Ni Octoate	Thermal	Ni Octoate	
THF	+10.5	+6.3	-3.5	-4.5	37.3	+10.7	-3.8	-10.4	-10.4	88.1
Methanol	+4.6	+14.8	-2.5	4.1	21.3	-5.5	+2.4	-7.6	-7.6	35.6
Isopropanol	+12.5	+6.9	-2.7	-4.6	17.0	+9.1	-2.4	-8.7	-8.7	38.6
DMSO	-20.0	-7.2	2.4	-1.9	110.0	-17.6	-26.2	-5.5	-5.5	175.0

## COMPARISON OF LOW-SEVERITY COAL PRETREATMENTS FOR SUBSEQUENT CATALYTIC LIQUEFACTION

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### ABSTRACT

Coal can be effectively solubilized by treatment with carbon monoxide reductant in an aqueous solvent (COsteam process). In recent work with U.S. and Australian low-rank coals, sodium aluminate was demonstrated to improve the conversions in the CO/H<sub>2</sub>O system and in water/hydrogen donor solvent mixtures. In this paper, the catalytic hydrotreatment of the solubilized low-severity products from sodium aluminate-catalyzed and uncatalyzed CO/H<sub>2</sub>O reactions of a Wyodak subbituminous coal are compared. Catalytic hydrogenations of the THF-soluble fractions obtained from the two low-severity products were performed with a conventional cobalt-molybdenum catalyst as well as two clay-supported iron catalysts at 425°C for 3 hours in the presence of 1000-psi (cold) H<sub>2</sub>O pressure. Liquefaction with the cobalt-molybdenum catalyst gave 68% conversion to heptane solubles for both the sodium aluminate and the uncatalyzed low-severity reaction intermediates. In contrast, the supported iron catalysts gave much higher conversions for the intermediate from the sodium aluminate-catalyzed reaction compared to those from the uncatalyzed reaction. These results have important implications for multistage liquefaction processing schemes.

Keywords: liquefaction catalysts, coal solubilization catalysts

### INTRODUCTION

Carbon monoxide and water have been utilized in the liquefaction of coal since 1921, when Fischer and Schrader demonstrated the effectiveness of this process (1). Improvements in the COsteam process have increased conversions to soluble products, but extensive depolymerization and hydrogenation of the coal macromolecules require further catalytic hydrotreatment of the COsteam product. The goal of the University of North Dakota Energy & Environmental Research Center (EERC) coal science group is the development of new homogeneous catalysts for the CO reaction. These catalysts are expected to aid in solubilization and preliminary reduction of low-rank coals to a high-quality intermediate product that can be easily catalytically converted to distillate fuels with low heteroatom content.

Catalysis of the first stage of coal liquefaction involves improving the rates of bond cleavage reactions leading to improved solubility and of preliminary reduction reactions so that oils and asphaltenes are produced without extensive retrogressive reactions. The catalysts should be able to interact effectively with the colloidal coal matter, to generate soluble products at moderate temperature. Thus various inexpensive and disposable inorganic agents that are soluble in the reaction vehicle or solvent are being investigated. Sodium aluminate catalyzed the solubilization of Australian coals in the CO/H<sub>2</sub>O system and in water/hydrogen donor solvent mixtures (2, 3). Previous work at the EERC demonstrated that aqueous sodium aluminate was also effective for Wyodak subbituminous coal (4). High conversions comparable to those obtained with hydrogen donor solvents and hydrogen sulfide

were obtained. This paper compares the suitability of the intermediates from catalyzed and uncatalyzed  $\text{CO}/\text{H}_2\text{O}$  reactions as a feed for catalytic hydrogenation.

## EXPERIMENTAL

### Catalyst Preparation

An Amocat-1A cobalt-molybdenum catalyst was presulfided by heating with a small amount of sulfur and 1000 psi of hydrogen in a 15-mL rocking microreactor heated at 350°C for 3 hours. The clay-supported iron catalysts were obtained from Universal Fuel Development Associates, Inc. and were in situ sulfided by adding a small amount of elemental sulfur with the catalyst prior to hydrotreating.

### Coal Solubilization

A slurry consisting of 5.0 g of coal (as-received Wyodak-Clovis Point), 2.5 mmole of  $\text{NaAlO}_2$  (if desired) dissolved in 3.0 g of water and 5.0 g of tetralin (solvent) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of carbon monoxide gas. The reactor was heated to 400°C in a rocking autoclave (initial heatup time = 11 minutes) and left at this temperature for 30 minutes. The reactor was cooled to room temperature, and the gases were removed. The products were distilled to remove water. The remaining slurry was extracted with THF. The THF-insoluble product was dried under vacuum and weighed. The percent conversion was calculated on the basis of the coal (maf) that did not appear in the THF-insoluble fraction. The extract was evaporated to remove THF. The resulting low-severity products from sodium aluminate-catalyzed (SA-LSW) and uncatalyzed reactions (U-LSW) contained the original tetralin as well as the solubilized coal material. These were stored under nitrogen for further catalytic hydrotreating.

The composition of THF-soluble products was determined by adding an aliquot of this product to a large excess of heptane with vigorous stirring. The heptane-insoluble product was separated by centrifugation, washed with heptane, dried in vacuo at 50°C, and weighed. The heptane-soluble product was evaporated to remove heptane and kept for further analyses. The heptane-soluble yield was calculated with the following equation:

$$\% \text{ heptane solubles}^* = \% \text{ conversion} - \% \text{ heptane insolubles}$$

(\* = includes gas and water)

### Catalytic Hydrotreatment of Low-Severity Intermediates

A slurry consisting of 3 g of SA-LSW or U-LSW, 10 wt% of desired catalyst, and 2 wt% of sulfur (if needed) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of hydrogen gas. The reactor was heated to 425°C in a rocking autoclave (initial heatup time = 15 minutes) and left at this temperature for 3 hours. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The product slurry was extracted with THF. The THF-insoluble product was dried under vacuum and weighed. The THF-insoluble fraction was used to determine the amount of coke formed due to retrogressive reactions during hydrotreatment. The extract was diluted to 250 mL with THF. A 4-mL aliquot of the THF-soluble was mixed with 1 mL of solution of internal standard (a mixture of 2,2,4-trimethylpentane and n-octadecane in dichloromethane) and analyzed by gas chromatography (GC). The remaining THF-soluble fraction was evaporated to remove THF, and the dark oil was added to a large excess of heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane, and dried in vacuo at 50°C. The percent conversion was calculated on the basis of

the heptane-insoluble product that was converted to heptane-soluble product (oils). The conversion and yield data are given in Table 1.

## RESULTS AND DISCUSSION

The advantage of using a solubilization stage in coal processing is that almost all of the inorganic material present in the coal can be eliminated prior to catalytic hydrogenation over a supported catalyst. Thus the calcium deactivation that has seriously affected catalytic liquefaction in the low-rank coals can be avoided. Aqueous solubilization reactions that utilize carbon monoxide as the reductant gas have been extensively investigated in this and other laboratories over many years (5-7). Basic catalysts have been employed to achieve higher conversions. The CO/H<sub>2</sub>O reduction has been shown to be superior to hydrogen for the first stage of liquefaction. A number of candidates for improving the conversion in CO/H<sub>2</sub>O were reported by Jackson and others (2, 3). Aqueous sodium aluminate gave good conversions of brown coal to oils at temperatures of 350° to 400°C. The mechanism for sodium aluminate activation of carbon monoxide to produce an effective reducing intermediate is still under investigation.

Investigations of homogeneous catalysts for coal liquefaction at the EERC (4) verified that sodium aluminate is also effective in improving the CO/H<sub>2</sub>O liquefaction of low-rank western U.S. coals. High conversions to THF solubles were obtained for the Wyodak subbituminous coal (89%). This was substantially higher than that obtained in a similar CO/H<sub>2</sub>O reaction with no added sodium aluminate (78%). Conversion of the Wyodak to THF solubles in a CO/H<sub>2</sub>O liquefaction experiment with sodium hydroxide catalyst was substantially lower (72%).

A mixed solvent containing an organic solvent with lower vapor pressure (tetralin) was also used for the CO/H<sub>2</sub>O reaction. Solubilization reactions of the Wyodak coal were performed in a water-to-tetralin wt/wt ratio of 0.6, both with and without sodium aluminate, at 400°C for 30 minutes with 1000 psi of cold initial CO pressure. Compared with water only, the operating pressure as well as conversions to THF-soluble products was significantly lower for the mixed solvent system. The sodium aluminate-catalyzed reaction gave 79% conversion to THF solubles, whereas the uncatalyzed reaction gave only 63% conversion. The lower yields for the mixed solvent in both catalyzed and uncatalyzed reactions may have resulted from the lower water concentration. The dependence of the conversions on the CO and water partial pressure was previously described (8). It should also be pointed out that the lower fluid density in the mixed solvent reactions may have resulted in a lower conversion. Higher conversions can be obtained by longer reaction times or higher temperatures, but minimal processing severity was desired for generating the intermediates needed for this study.

The yield of heptane solubles from the sodium aluminate-catalyzed reaction (CO/water/tetralin system) was the same (30% heptane solubles) as that obtained in uncatalyzed reactions in the same system (31% heptane solubles). Since the conversions were higher for the sodium aluminate-catalyzed reactions, the heptane-insoluble fraction is larger for the sodium aluminate-catalyzed reactions. Thus the two products do not have the same composition with respect to the solubility fractions.

Development of an economical process for liquefaction of low-rank coals requires an evaluation of the suitability of the soluble COsteam products as a feed for catalytic

hydrogenation. The catalytic hydrogenation is required for depolymerization to a distillable product with higher hydrogen content and low heteroatom content. The evaluation of product quality was determined by carrying out hydrogenations with both a conventional supported cobalt-molybdenum catalyst as well as two dispersed iron sulfide catalysts. In these tests, the THF-soluble low-severity products from the sodium aluminate-catalyzed (SA-LSW) and the uncatalyzed CO/H<sub>2</sub>O reactions (U-LSW) were catalytically hydrotreated with 10 wt% of the catalyst at 425°C for 3 hours in hydrogen (1000 psi cold). Since the compositions of the U-LSW and SA-LSW were not identical, the percent conversion was measured as the percentage of heptane insolubles converted to heptane solubles in the hydrogenation of each intermediate with each catalyst. The conversion data and product yields are given in Table 1.

The thermal (nuncatalytic) hydrogenation of the SA-LSW product converted 24% of the heptane-insoluble fraction to heptane solubles. Thermal hydrogenation of the U-LSW product gave a similar conversion to heptane solubles (26%).

The supported cobalt-molybdenum catalyst was presulfided in hydrogen sulfide/hydrogen (10% H<sub>2</sub>S). Hydrogenation of the SA-LSW with the presulfided cobalt-molybdenum catalyst resulted in a high conversion (68%) of the heptane-insoluble fraction to heptane solubles. Hydrogenation of the U-LSW with this catalyst also gave a high conversion to heptane solubles (67%).

In contrast to the molybdenum catalyst results described above, the results obtained with sulfided iron catalysts demonstrated significant differences for the hydrogenation of the low-severity products obtained from the sodium aluminate-catalyzed and the uncatalyzed reactions. An iron/alumina-pillared montmorillonite catalyst was sulfided in situ by adding elemental sulfur to the reactants. The hydrogenation of SA-LSW with this catalyst gave a 62% conversion to heptane solubles. A conversion of only 47% was obtained with the U-LSW product. The very large increase in conversion to heptane-solubles in the SA-LSW experiment clearly demonstrates that the use of sodium aluminate catalyst in the CO/water pretreatment solubilization stage had a beneficial effect on the quality of the low-severity product.

This improvement in the hydrotreatability of the low-severity product as a result of sodium aluminate catalysis was further demonstrated by a different sulfided iron catalyst. This catalyst was prepared by the impregnation of triiron complex on an acid-washed montmorillonite. Sulfidation was performed in situ with elemental sulfur, and reaction conditions were the same as before. The reaction with the SA-LSW gave an excellent conversion to heptane solubles (67%), which compared favorably with that produced by the molybdenum catalyst. As in the reactions with the pillared clay-supported iron sulfide catalyst, the reaction of this clay-supported iron catalyst gave a much lower conversion (56%) with the U-LSW.

## CONCLUSIONS

The low-severity products from CO/H<sub>2</sub>O reactions obtained with and without sodium aluminate were compared in hydrogenation tests with three catalysts as well the thermal nuncatalytic reaction. The thermal reaction gave poor conversions to heptane solubles for both low-severity products. A significant difference in the conversions of the two low-severity products to heptane solubles was found for two clay-supported iron catalysts. The sodium

aluminate-catalyzed CO/H<sub>2</sub>O reaction gave a product with much higher potential for hydrotreating than that obtained from the uncatalyzed CO/H<sub>2</sub>O reaction. In contrast, a commercial cobalt-molybdenum catalyst gave about 68% conversion for both low-severity products. Thus the very effective hydrogen-activating molybdenum sulfide catalyst was able to compensate for the lower quality of the uncatalyzed reaction product. If the economics of coal liquefaction and catalyst recovery demand the use of the inexpensive and disposable iron catalysts, the use of sodium aluminate in a pretreatment solubilization step will be very important in increasing the yields obtained in the subsequent catalytic hydrogenation step.

#### ACKNOWLEDGMENTS

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Table 1

Catalytic Hydrotreating of Low-Severity Products  
from CO/H<sub>2</sub>O Liquefaction of Wyodak Coal

Reaction Time = 3 hr, H<sub>2</sub> = 1000 psi (cold),  
Low-Severity Product wt = 3 g, Catalyst wt = 0.3 g

Low-Sev. Product	Catalyst	Sulfur (%)	Temp. (°C)	Heptane Insol.	%-Conv. to Heptane Sol.
U-LSW	---	---	---	0.49	---
U-LSW	None	None	425	0.36	26
U-LSW	APC-Fe <sub>3</sub> <sup>a</sup>	(2)	425	0.26	47
U-LSW	K-10/Fe <sub>3</sub> <sup>b</sup>	(2)	425	0.22	56
U-LSW	Co-Moly	(2)	425	0.16	67
SA-LSW	---	---	---	0.61	---
SA-LSW	None	None	425	0.48	24
SA-LSW	APC-Fe <sub>3</sub> <sup>a</sup>	(2)	425	0.23	62
SA-LSW	K-10/Fe <sub>3</sub> <sup>b</sup>	(2)	425	0.20	68
SA-LSW	Co-Moly	(2)	425	0.20	68

<sup>a</sup> Catalyst washed with ethanol prior to drying and calcination.

<sup>b</sup> Triiron was supported on K-10 in ethanol.

SA-LSW = Sodium aluminate-catalyzed low-severity product.

U-LSW = Uncatalyzed low-severity product.

PARAMETRIC EVALUATION OF LOW TEMPERATURE CO PRETREATMENT OF  
SUBBITUMINOUS COAL

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Keywords: Coal liquefaction, carbon monoxide, pretreatment

**Abstract**

Thermal CO pretreatment of subbituminous coal in aqueous media at 250-300°C produces a water-insoluble product having a higher hydrogen content, lower oxygen content, increased solubility and higher volatility. Both the conversion and water-gas-shift (WGS) reactions are catalyzed by  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , although under some conditions significant WGS reaction is not accompanied by comparable modification to the coal structure. Turnover numbers in the NaOH-catalyzed WGS reaction in excess of 100 were observed. Thermal, optical and chemical characterization data on the modified coal is presented. Improved liquefaction conversion and oil yields of the pretreated material were observed relative to the corresponding untreated coal.

**Introduction**

Earlier work has shown that pretreating coal can impact on its performance in subsequent processing to provide higher yields and better product slates.<sup>1</sup> Pretreatment can contribute toward lowering the processing costs of converting coal to liquid fuels. The application of CO in conversion of coal in aqueous media was pioneered by Fischer and Schrader<sup>2</sup> and later revived by Appell and co-workers.<sup>3</sup> They found that the  $\text{CO}/\text{H}_2\text{O}$  system is effective for converting low-rank coals to liquid products via the WGS reaction along with removal of heteroatoms (particularly oxygen).<sup>4</sup>

Previously, we reported that pretreating a subbituminous coal with CO in an aqueous media at 300°C produces a material which has a higher atomic H/C ratio, lower oxygen content, higher pyridine solubility and a liquefaction reactivity comparable to untreated coal.<sup>5</sup> As an extension of the preceding study, the effect of temperature, NaOH concentration and CO pressure on pretreatment was evaluated and the effect of adding different salts ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ) on the reaction was studied. In addition, the liquefaction of the pretreated coal was determined.

**Experimental**

Coals - Ultimate analyses of Clovis Point and Black Thunder Wyodak coals, that had been ground to -200 mesh, riffled and stored in tightly sealed containers, are given in Table 1.

Procedures - Microautoclave coal pretreatment and liquefaction experiments were performed in 25 ml reactors which, after loading and pressurizing, were submerged in a fluidized sand bath at reaction temperature and agitated vertically at a rate of 400 cycles per minute. After quenching, gaseous products were collected and analyzed. In coal pretreatment experiments solid and liquid products were scrapped and washed from the reactor with water and then filtered and air dried at 4°C. These products were separated into the THF insoluble, THF soluble/pentane insoluble (PA+A), and pentane soluble fractions. The difference between the weight of coal charged to the reactor and the sum of the THF insolubles plus PA+A is reported as oil+gas+water (OGW).

In the liquefaction experiments solid/liquid products were separated into THF insoluble, PA+A, and pentane soluble (oil+water) fractions. Conversions and product yields are reported on a moisture and ash free (maf) basis assuming complete recovery of ash in the THF insolubles. Further details of the experimental work-up procedure have been reported elsewhere.<sup>5</sup> Larger scale coal pretreatments were performed in a 1-liter stirred autoclave by adding 80 ml. of water to the reactor which was sealed and pressurized with CO to 800 psig. The reactor was heated to  $310 \pm 5^\circ \text{C}$  and a slurry containing 150 g dry coal in an additional 120 ml water, containing the required amount of NaOH or  $\text{Na}_2\text{CO}_3$ , was injected into the hot reactor. After approximately 7-8 minutes, the temperature of the reactor had returned to the reaction temperature. After 1 hour the reactor was cooled and depressurized and the solid product was removed from the reactor and separated in the manner described above. Analysis - Optical microscopic techniques are discussed elsewhere.<sup>5</sup> Both as-received and CO-pretreated Black Thunder coal were analyzed simultaneously by thermogravimetry/differential thermal analysis/differential thermogravimetry (TG/DTA/DTG) on a Seiko TG/DTA 320. The conditions were: heating rate of  $10^\circ\text{C}/\text{min}$  from ambient temperature to  $120^\circ\text{C}$ ; a 15 min hold at  $120^\circ\text{C}$  to remove surface moisture; a heating rate of  $10^\circ\text{C}/\text{min}$  from  $120^\circ\text{C}$  to  $600^\circ\text{C}$ ; He sweep rate of 200 ml/min; and constant sample volume weighing approximately 20 mg.

#### Results and Discussion

CO Pretreatment - Experiments to define the effects of temperature, CO pressure, and NaOH concentration on conversion and product distribution were organized in a  $2^3$  factorial format as shown in Table 2. The experiments were organized around low and high levels for each of the independent variables, i.e., temperatures of  $250^\circ\text{C}$  and  $300^\circ\text{C}$ , starting CO pressures of 300 and 800 psig, and NaOH molar concentrations of 0.021 and 0.33. Results from these experiments show that the yield of THF soluble product is substantially higher at  $300^\circ\text{C}$  than at  $250^\circ\text{C}$ , irrespective of the initial CO pressure and NaOH concentration. From the magnitude of the THF conversions at  $300^\circ\text{C}$ , there appears to be an interactive effect of NaOH concentration and CO pressure. THF conversions for three of these four runs are in excess of 23 wt% while the other at 300 psig CO and 0.021M NaOH gave a somewhat lower THF conversion. The magnitude of the THF soluble products at  $250^\circ\text{C}$  is quite small but uniform and fail to show any definite trend in their distribution. The effectiveness of the CO-pretreatment at the lower NaOH concentrations is encouraging since it shows that the base concentration can be reduced.

The results observed earlier<sup>5</sup> plus those reported here show that humic acids (HA) are observed only at  $300^\circ\text{C}$  and at CO pressures (cold) of 400 psig or less. Likewise, at 300 psig CO, HA is favored by increasing NaOH concentration. This agrees with previous studies which showed that the HA yield is dependent primarily on reaction temperature, pH and reaction time.<sup>6</sup> HA appears to diminish as PA+A increases and its disappearance parallels an increase in the H/C ratio in the water insoluble product.

In most cases, especially at higher CO pressures, coal dissolution reports to the PA+A fraction rather than the OGW fraction. However, as our previous results on Clovis Point Wyodak coal showed, treatment at low CO pressures, such as in the presence of 200 psig CO or in the absence of CO, i.e., in  $\text{N}_2$ , results in formation primarily of OGW

product.<sup>5</sup> The resulting pretreated products have lower H/C ratios, i.e., 0.72 and 0.75 in the presence of 200 psig CO and in the absence of CO, respectively, relative to coal, which has a H/C ratio of 0.83. The H/C ratio for the 800 psig CO-pretreated product was 0.92. The products prepared at low CO pressures are significantly more intractable with pyridine compared to products prepared at 800 psig CO. The pyridine extract yields (wt. maf basis) were 4% for untreated coal, 6% for coal treated in the absence of CO (in N<sub>2</sub>), 9% for coal treated with 200 psig CO, and 60% for coal treated with 800 psig CO. Optical microscopy showed that the coal treated at 800 psig CO pressure underwent significant modification relative to the original coal.

In general, temperature appears to have little impact on the extent of the WGS reaction. The maximum WGS conversion obtained in this series was 88%, which experimentally confirms that the reaction is not thermodynamically limited. However, CO conversion appears to plateau at approximately 50% in the higher temperature and pressure experiments. Extending the reaction period to two hours increased CO conversion by only 5%. Similar limitations on CO conversions have been reported in the reaction with NaOH to make sodium formate.<sup>7</sup>

Hydrogen that is generated by the WGS reaction and then apparently consumed in the reaction is higher at 800 psig CO (18-20 mg/g maf coal) than observed at 300 psig (ca. 10 mg/g maf coal). This disappearance or "consumption" of hydrogen that occurs at 250°C has not been correlated to either coal reconstruction or an increase in the H/C ratio in the product. We are investigating whether this hydrogen is being "stored" in one of the WGS reaction intermediates (e.g. Na formate, formic acid, etc.) as proposed by Elliott<sup>8</sup> and others.<sup>9</sup> Unquestionably, base catalyzes the disappearance of CO and formation of H<sub>2</sub> by the WGS reaction. The molar ratio of CO converted per mole of NaOH initially present in the experiments with 0.021M NaOH varies between 96 and 183:1, while for those experiments at 0.33M the ratio varies from 9 to 12:1. Although WGS conversions are higher at the lower pressures, turnover numbers increase at higher CO pressures.

Comparative conversions and product distributions from CO pretreatment in 0.33M solutions of NaOH, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub> are shown in Table 3. Even though the pH of the starting NaHCO<sub>3</sub> (pH ~ 8.5) solution is significantly lower than that of the NaOH or Na<sub>2</sub>CO<sub>3</sub> solutions (pH >13), they all catalyze the WGS reaction to a similar extent. Likewise, the relative THF solubilities as well as the optical microscopic properties of the water insoluble products are quite similar. Clearly, HCO<sub>3</sub><sup>-</sup> is effective in promoting both the WGS reaction and the corresponding pretreatment of coal.

The volatilization of the water insoluble product is considerably higher than for the coal itself as shown by TGA (Figure 1a). In addition, the temperature of maximum volatilization decreases from 442°C for untreated coal to 432°C and 429°C for Na<sub>2</sub>CO<sub>3</sub> and NaOH treated samples, respectively (Figure 1b). This suggests a reduced molecular weight distribution.

**Liquefaction** - CO-pretreated coals gave better THF conversion than untreated coal under mild liquefaction conditions (see Table 4). The increased conversion from both the NaOH and Na<sub>2</sub>CO<sub>3</sub> catalyzed water insoluble products reported almost exclusively to the PA+A fraction. Catalyzed liquefaction in the presence of both NiMo/alumina (Shell 324)

and nanometer size iron oxide (Nanocat®) provided even sharper differentiation of the pretreated coal versus the untreated coal as shown in Table 5. The NiMo catalyst added at a level of 0.1 wt% Mo on dry coal increased oils+water conversion by 10 wt% and iron oxide added at a level of 1 wt% on dry coal increased conversion by 5 wt% and oils+water conversion by 7 wt%. All of the pretreated coal runs show a decrease in gases production and a lower H<sub>2</sub> consumption than for untreated coal. Presumably, the lower oxygen content in the pretreated coal would reduce the water portion of the oils+water fraction.

### Conclusions

Temperature is the dominant independent variable in the CO-pretreatment of subbituminous coal with a significant interactive effect at 300°C between CO-pressure and NaOH concentration. NaOH concentrations as low as 0.021M were found to be effective in promoting both the WGS reaction and in pretreating the coal. NaHCO<sub>3</sub> was found not only to be effective in promoting the WGS reaction but also in giving water-insoluble product that is comparable to water-insoluble product from NaOH and Na<sub>2</sub>CO<sub>3</sub> catalyzed CO-pretreatment. The volatility of the product increases versus untreated coal. In addition, the temperature decreases at which maximum volatilization occurs. Catalyzed liquefaction of CO-pretreated coal gives increased THF conversion and oil yield plus better H<sub>2</sub> utilization compared to untreated coal.

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Table 1. Ultimate Analysis of Wyodak Coals		
	Clovis Point	Black Thunder
Composition, wt% maf		
Carbon	71.0	73.9
Hydrogen	4.9	5.2
Nitrogen	1.3	1.3
Sulfur	1.1	0.6
Oxygen, by difference	21.7	19.0
Ash, wt% dry coal	6.94	6.12
H/C Ratio	0.83	0.84

Table 2. Product Distribution from CO Pretreatment of Black Thunder Coal <sup>a</sup>								
Condition <sup>b</sup>	LLL	HLL	LHL	HHL	LLH	HLH	LHH	HHH
Temp, °C	250	300	250	300	250	300	250	300
CO, psig <sup>c</sup>	300	300	800	800	300	300	800	800
NaOH, mol/l	0.02	0.02	0.02	0.02	0.33	0.33	0.33	0.33
THF Conv	5	16	6	23	7.4	26	9	32
PA+A	3	8	2	18	7.5	18	9	29
Humic Acids	-	1	-	-	-	4	-	-
O+G+W	2	7	4	5	-	4	-	3
WGS Shift <sup>d</sup>	58	56	36	41	n.a. <sup>e</sup>	88	45	45
H <sub>2</sub> Consump, mg/g maf coal <sup>f</sup>	10	9	18	20	n.a.	6	20	20
<p>a. 25 ml reactor; 1 hour reaction time; 2 grams dry coal; 20-22 wt% moisture; 3.25 g water/g maf coal; all conversions and yields based upon maf coal.</p> <p>b. L = low, H = high; sequence: temperature, CO pressure, NaOH concentration.</p> <p>c. CO pressure (cold).</p> <p>d. <math>\text{WGS Conv}(\%) = ([\text{CO}_{\text{in}}] - [\text{CO}_{\text{out}}]) / [\text{CO}_{\text{in}}]</math></p> <p>e. n.a., not available</p> <p>f. <math>\text{H}_2 \text{ Consump (mg/g maf coal)} = [\text{H}_2(\text{from WGS})] - [\text{H}_2(\text{final})]</math></p>								

Table 3. Effect of Na Salt on CO-Pretreatment of Wyodak Coal <sup>a</sup>			
Catalyst	NaOH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>
Coal <sup>b</sup>	BT	BT	CP
THF Conv.	32.0	37.2	36.0
Product Distribution, wt% maf coal			
PA+A	29.0	29.5	31.1
Oils+Gas+Water	3.0	5.7	4.9
WGS Reaction <sup>c</sup>	45	47	51
H <sub>2</sub> Consump, g/g maf coal <sup>d</sup>	20	22	24
Pyridine Solubles <sup>e</sup>	60	56	n.a. <sup>f</sup>
a. Conditions: 800 psig CO with 5.5 ml of 0.33M Na salt solution, 300°C, 1 hr. b. BT is Black Thunder Wyodak coal; CP is Clovis Point Wyodak coal. c. $WGS\ Conv(\%) = ([CO_{in}] - [CO_{out}]) / [CO_{in}]$ d. $H_2\ Consump\ (mg/g\ maf\ coal) = [H_2(\text{from WGS})] - [H_2(\text{final})]$ e. Wt% of water-insoluble product. f. n.a. not available			

Table 4. Liquefaction of Base Promoted CO-Pretreated Coal <sup>a</sup>			
	Na <sub>2</sub> CO <sub>3</sub>	NaOH	Untreated
THF Conversion	80.4	80.4	74.7
Product Distribution, wt% maf coal			
PA+A	53.4	50.6	43.9
Oil+water	24.3	30.0	26.1
Gases	2.7	2.0	4.7
H <sub>2</sub> Consump, mg/g maf coal	17.8	18.6	21.4
Total H <sub>2</sub> Consump, mg/g maf coal <sup>b</sup>	27.3	27.1	34.2
a. 400°C, 2 g dry coal/2 g tetralin, 1 hr, 800 psig H <sub>2</sub> (cold), 25 ml reactor. b. Includes hydrogen from tetralin solvent.			

Table 5. Catalyzed Liquefaction of CO-Pretreated Coal <sup>a</sup>				
	Pretreated Coal <sup>b</sup>		Untreated Coal	
	Shell 324 <sup>c</sup>	Nanocat <sup>d</sup>	Shell 324 <sup>c</sup>	Nanocat <sup>d</sup>
Added Fe, wt% dry coal	-	1.0	-	1.0
Added Mo, wt% dry coal	0.1	-	0.1	-
THF Conv, wt% maf coal	84	86	83	81
Product Distribution, wt% maf coal				
PA+A	43	52	49	50
Oils+Water	39	32	29	25
Gases	2	2	5	6
Total H <sub>2</sub> Consump, mg/g maf coal <sup>e</sup>	31	29	34	34
a. Liquefaction conditions: 400°C, 2 g dry coal/2 g tetralin, 1 hr, 800 psig H <sub>2</sub> (cold), 25 ml reactor. b. Pretreated coal prepared in 1-liter autoclave with 0.19M Na <sub>2</sub> CO <sub>3</sub> (3.7 wt% maf coal), 800 psig CO, 310±5°C. c. NiMo/alumina (2.8 wt% Ni, 12.4 wt% Mo) ground to -100 mesh; dimethyldisulfide added to provide a S/added metal(s) (mol/mol) ratio of 2. d. 63 wt% Fe. e. Includes hydrogen from tetralin solvent.				

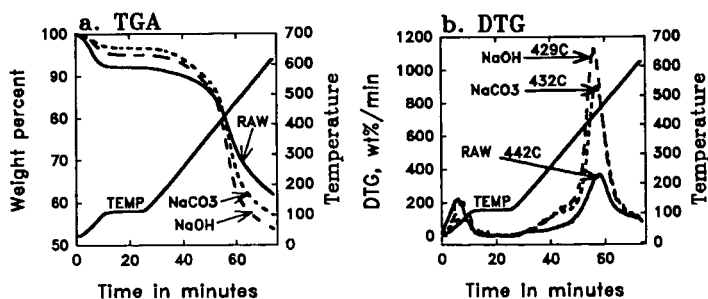


Figure 1a,b. Thermal analysis of CO-pretreated coals.

## IMPROVED LIQUEFACTION OF LOW RANK COALS BY REDUCTION OF RETROGRESSIVE REACTIONS

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**KEYWORDS:** Coal liquefaction, Low rank coals, Retrogressive reactions

### INTRODUCTION

Direct coal liquefaction processes have recently been based on a two stage processing approach: coal dissolution followed by upgrading of the solubilized products. While low rank coals offer the potential of high oil yields because of their small aromatic ring cluster size, low rank coals are more difficult to liquefy in the first (solubilization) stage (1,2) under conditions optimized for bituminous coals. For example, Whitehurst and co-workers (3-5) demonstrated that low rank coals produce low conversions in short contact times in a donor solvent (see Fig. 1) or for long times in a non-donor solvent. For low rank coals and lignites, it appears likely that crosslinking reactions associated with oxygen functional groups (6,7) occur before the homolytic cleavage reactions, and if not controlled can limit the maximum conversion of coal to liquids. This paper discusses three approaches which have been used to either study or mitigate these reactions in an effort to improve liquefaction yields from low rank coals. 1) catalytic pretreatment; 2) demineralization and cation-exchange; 3) hydrothermal pretreatment and water addition.

### RESULTS AND DISCUSSION

#### Catalytic Pretreatment

**Impregnated Catalysts** - For low rank coals, the use of a pretreatment at 350°C with an impregnated  $\text{MoS}_2$  catalyst and  $\text{H}_2$  shows a vastly superior product slate in subsequent liquefaction at 425°C (8-14). The improvement is especially noticeable for the low rank coals where short contact time liquefaction alone produces large residues (3-5). Results obtained at Advanced Fuel Research, Inc. (AFR) (15-17) confirmed the observations of Derbyshire and co-workers (8-14). Data for a Wyodak subbituminous coal (PSOC-1401) are presented in Fig. 2. The figure compares liquefaction data (10 min at 425°C) for no preliquefaction, preliquefaction at 275°C (with  $\text{H}_2$  and catalyst) and preliquefaction at 350°C (with  $\text{H}_2$  and catalyst). The results show that preliquefaction at 350°C does have a positive effect on the total yield and product quality in liquefaction (much lower residue) while preliquefaction at 275°C causes a negative effect (higher residue).

A number of tests were performed on the preliquefaction products to identify the chemistry, including FT-IR analysis of the Wyodak coal preliquefaction residue (15-17). The preliquefaction step produces the following changes in the residue: 1) decreases the carbonyl ( $1700\text{ cm}^{-1}$ ) and hydroxyl regions ( $3400\text{ cm}^{-1}$ ) (presumably carboxyl loss); 2) decreases the aliphatic hydrogen ( $2900\text{ cm}^{-1}$ ); and 3) substantially increases the aromatic hydrogen ( $750\text{-}850\text{ cm}^{-1}$ ). Our initial conclusion from the FT-IR data on the residual is that it is the reduction in the carboxyl concentration which is most important to the improvements brought about by preliquefaction, and this reduction requires the catalyst but not the solvent and probably not the hydrogen. The increase in aromatic hydrogen appears to be due to the adduction of naphthalene.

The evolutions of the volatile products of pyrolysis are related to the functional group composition of the sample, so TG-FTIR analysis provides a good complement to the FT-IR functional group analysis. Since the FT-IR analysis showed the carbonyl region to change drastically in preliquefaction, we considered the CO<sub>2</sub> evolution which is probably associated with the thermal decomposition of the carboxyl groups (15-17). When a comparison was made of the CO<sub>2</sub> evolution from a number of residues, the major changes were observed for catalytic preliquefaction at 350°C with hydrogen or nitrogen. Here a drastic reduction is observed in the CO<sub>2</sub> evolution at all temperatures. This result is consistent with the major chemical change in the carboxyl groups observed from the FT-IR results. The nitrogen thermal case shows much less of a change.

Since the preliquefaction showed a significant role of carboxyl groups, model compounds with aryl carboxyl groups were studied. The starting reaction mixture used was 50% naphthalene, 25% of 1-naphthoic acid and 25% of 2-naphthoic acid (weight basis). The FT-IR spectra of the starting reaction mixture and the residue after preliquefaction indicated that there is a strong loss in the carbonyl and hydroxyl bands during the preliquefaction in the presence of the catalyst. A blank run was done without the catalyst which indicates that the catalyst is necessary to cause extensive decarboxylation.

Recently, a set of experiments was done with fresh Argonne Wyodak coal impregnated with a molybdenum sulfide catalyst prepared by the incipient wetness technique (18). This was a repeat of earlier work done by Derbyshire and co-workers (8-14) and Solomon and co-workers (15-17) discussed above, except for the substitution of the Argonne Wyodak coal for the PSOC 1401 Wyodak coal. The results are shown in Fig. 3 for freshly opened and aged samples. This treatment did not show an improvement of the liquefaction yields for the fresh Argonne Wyodak coal samples. It was concluded that this different behavior toward catalyst impregnation may be due to aging of the PSOC 1401 Wyodak coal, which was presumably absent for the Argonne coal. Consequently, similar experiments were done with a sample of the latter coal which had been stored in a dry box, but where no care was taken to exclude air. The liquefaction results for the aged samples, with and without catalyst are also shown in Fig. 3. As expected, the yield of THF solubles was reduced by aging of the coal and these yields were subsequently improved by catalyst addition. However, a surprising result was that the addition of catalyst to the aged samples gave yields that were even higher than for the fresh coal or the catalytically treated fresh coal. Similar results have recently been reported by Schobert and coworkers for an air dried DECS-8 Wyodak subbituminous coal (19). The results for gas evolution from these samples during pretreatment and liquefaction are given in Fig. 4. The catalyst reduces the amount of CO<sub>2</sub> evolved during the pretreatment stage for both the fresh and oxidized coals. However, only in the case of the oxidized coals did the reduction in early CO<sub>2</sub> (and, presumably, the associated crosslinking reactions) lead to improvements in liquefaction yields.

A possible explanation for the above results is as follows. The mild oxidation of the coal due to aging may create positively charged sites which attract the tetrathiomolybdate anions during the impregnation process, which leads to better dispersion of the catalyst.

**Ion-Exchanged Catalysts** - To increase yields with fresh coals there are two approaches which can be pursued: a) to find a better catalyst to be impregnated onto the coal matrix; or b) to find a technique to get better - if possible atomic - dispersion of the catalyst. There has been a significant effort in the literature in pursuit of both approaches, however, a reliable and simple technique resulting in atomic dispersion of an active catalyst still needs to be found.

Ion exchange experiments have demonstrated that, around neutral pH, the coal surface is negatively charged, thus preventing anions from adsorption or ion exchange (20). This can be overcome in acidic media but any acidic treatment will result in removal of cations - an effect leading to enhanced liquefaction itself (21-25). This would obscure the effect of a catalyst. In order to circumvent this problem our approach was to first react the coal with trivalent cations

(Fe<sup>+3</sup>) and thus produce locally positively charged sites (18). After this pretreatment, the tetrathio-molybdenate anions could be anchored to these positions. This technique worked very well and it was also found that the catalyst activity thus prepared depended on the Fe/Mo ratio. Since no H<sub>2</sub> pressure was applied in the liquefaction, H<sub>2</sub> evolution could be observed occasionally, but only in cases of catalyzed liquefaction. The occurrence of H<sub>2</sub> thus was the indicator of catalytic activity in the system towards hydrogenation-dehydrogenation with the actual H<sub>2</sub> concentration depending on the ratio of the two reaction rates. Table 1 shows a comparison of the time resolved liquefaction yields for a catalyzed versus uncatalyzed run for one of the most active formulations (1.4% Fe/0.6% Mo). The advantage of the catalysis is more evident at earlier reaction times, as would be expected.

### **Modification of Liquefaction Chemistry by Demineralization or Cation-Exchange**

**Coal modifications to remove cations** - Crosslinking has also been observed to be influenced by the presence of alkali metals, whose removal increases pyrolysis tar yields (26) and fluidity (27). These results would indicate that the role of carboxyl groups, as indicated above, is important, but it is the carboxylate (cation exchanged carboxyls) which are the key agents in retrogressive reactions for low rank coals. The role of calcium in reducing liquefaction yields from low rank coals has been suggested in previous work by Whitehurst et al. (4), Mochida et al. (28), and Joseph and Forrai (29). It is also consistent with work which shows an effect of calcium on reducing pyrolysis tar yields (26,30-33). The role of calcium may be to provide a nascent crosslink site in the coal by allowing coordination of groups like carboxyl and hydroxyl which are prone to such reactions. Otherwise, these sites would be more likely to coordinate with water (through hydrogen bonding) than with each other.

The preparation of modified low rank coals was studied systematically by Serio et al. (21-25). The following coal modifications were tested: raw, vacuum dried, treated with ammonium acetate, acid-demineralized and methylated. Each of the latter three modifications was effective in removing ion-exchanged cations. The results of liquefaction experiments with the coals and modified coals are summarized for the Zap lignite in Fig. 5. The results for the Wyodak subbituminous coal (not shown) are similar to those for the Zap lignite (22). The results show that the decrease in crosslinking, as implied by the reduction in CO<sub>2</sub> yield (Fig. 5b), roughly correlates with the increased liquefaction yields (soluble products, Fig. 5a). The trends in CO<sub>2</sub> yield (inverse correlation) and solubles from liquefaction (positive correlation) generally parallel the results from pyrolysis for the tar yield (Fig. 5c). The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal, presumably because of the lack of exchangeable cations. A similar beneficial result has recently been observed by Miller et al. (34) in liquefaction studies with the Argonne Wyodak coal treated with methanol/HCl.

TG-FTIR analyses were run on the modified coals to see whether changes occurred in the gas evolutions. The results indicated that the demineralization and methylation processes both decrease the evolution of CO<sub>2</sub> and H<sub>2</sub>O between 200°C and 400°C where crosslinking occurs, suggesting that the high tar and liquid yields produced by these two treatments are a result of reduced crosslinking which is accompanied by reduced evolutions of CO<sub>2</sub> and H<sub>2</sub>O.

**Coal Modifications to Add Cations** - Recent work at AFR has involved preparation of ion-exchanged (barium, calcium, and potassium) coals starting with demineralized Argonne Zap, and Wyodak samples (21, 25). The exchange was done at two different pH levels (8 and 12.5) in order to effect exchange of carboxyl groups and carboxyl plus phenolic groups, respectively. These modified samples were subjected to functional group analysis as KBr pellets with FT-IR, programmed pyrolysis with TG-FTIR, and donor-solvent liquefaction experiments. The results of sample characterization by programmed pyrolysis at 30°C/min to 900°C or solvent extraction/solvent swelling experiments in pyridine are summarized in Table 2 for the Zap lignite.

These results show that demineralization tends to increase the tar yields and decrease the gas yields, which is consistent with the previous work discussed above. Similar results were observed for the Wyodak coal (21). Table 2 also shows a decrease of the tar yield with the extent of ion-exchange with the metal cations, and a corresponding increase in the total amount of gas evolution. The liquefaction results for the different samples are shown in Table 3. The data in Tables 2 and 3 show that the yields of both the pyrolysis tar and toluene solubles from liquefaction decrease with the extent of ion-exchange, i.e., in the order of (demineralized) > (ion-exchanged at pH 8) > (ion-exchanged at pH 12.5). This result indicates that having the carboxyl or phenolic groups in the salt form makes it easier to crosslink the coal structure during pyrolysis or liquefaction reactions. The ability of cations to coordinate polar groups is probably an important aspect of their role in retrogressive reactions. The ability of both monovalent and bivalent cations to act as initial crosslinks in the structure is supported by data on the volumetric swelling ratios (VSR) in pyridine and the yields of pyridine extractables, also shown in Table 2. The values of the VSR are lower for the bivalent cations at high pH. At pH 8, the values of the VSR for the monovalent and bivalent cations are more similar, though lower than the values for either the raw or demineralized coals. Consequently, the evidence indicates that the monovalent cations can also act as crosslinking agents, although this must occur through electrostatic rather than covalent interactions. It makes sense that valency would be less important in the normal state of the coal or at pH=8 since, for steric reasons, cations are unlikely to be exchanged on more than one carboxyl or ortho-dihydroxy site.

#### **Hydrothermal Pretreatment and Water Addition**

**Hydrothermal Pretreatment of Coal** - Water pretreatment of coal at elevated temperatures, has been studied previously as a means to increase the yields of liquid products from extraction (35,36), pyrolysis (36-38), or liquefaction (39,40) of coal. Selected results from work done at AFR with Zap coal are shown in Fig. 6 (37,39). The data show that the sharp increase of pyrolytic tar yield, as a result of short time water pretreatment, is accompanied with decreased pyrolysis CO<sub>2</sub> evolution. This is in harmony with our previous conclusions about the correlation between decomposition of oxygen functionalities and crosslinking, namely the water pretreatment apparently removes precursors which would otherwise lead to crosslinking under liquefaction conditions. The pyrolysis data for the water pretreated samples show a close similarity for water pretreatment to accelerated aging of the coal (38). However, the toluene solubles of a subsequent liquefaction are reduced opposite to our expectations (see Fig. 6d). Another observation was that, specifically in this short pretreatment time range, occasionally negative oil yields were observed (39). Since the oils are measured by weight difference a likely explanation is that the solvent is forming adducts with the pretreated samples. The water pretreatment step appears to sensitize the coal to this problem.

**Pyrolysis and Liquefaction of Moisturized Coal Samples** - Remoisturization of vacuum dried Zap and Wyodak was done in the attempt to understand if moisture uptake for low rank coals is a reversible process and to see if moisture influences the role of the cations. The remoisturized samples were analyzed by programmed pyrolysis with TG-FTIR. Preliminary results show that the moisture content can be restored to values which are close to those of the raw coals, especially for Zap (21,25).

The detailed results for the pyrolysis and liquefaction experiments are given in Ref. 21. In general, pyrolysis tar yields and the toluene solubles yields from liquefaction for the remoisturized samples were similar to those for the vacuum dried samples. It appeared that the liquefaction results were more sensitive to the presence of moisture, although the increases in asphaltene yields were generally balanced by decreases in oil yields. A possible explanation for the difference is that most of the moisture is depleted early in the pyrolysis process, whereas the moisture is retained in the reactor during liquefaction and can exist in a liquid phase under the right conditions.

**Water Addition to Liquefaction Experiments** - It is also known from our results (21) and the literature (41) that the moisture is associated with cations in raw coals. Consequently, an investigation was made to determine if the deleterious effects of cations could be mitigated by adding water to the donor solvent liquefaction system. Results from experiments with raw and demineralized Zap at three different temperature levels are given in Table 4. At temperatures near or below the critical temperature of water (374 °C), it appears that there is a profound beneficial effect of added water for the raw coal (note the significant reduction in CO<sub>2</sub> evolution). Conversely, there is a significant deleterious effect of added water for the demineralized coals. The ability of water to interact with cations and affect the course of the thermal decomposition behavior is consistent with results that have been observed in hydrothermal treatment of coal, which mimics the geological aging process in many respects.

## CONCLUSIONS

The conclusions from this study are as follows:

- Catalytic pretreatment (Mo impregnation following by heating to 350 °C for 30 min.) prior to liquefaction leads to increased yields for low rank coals which have not been protected from aging, but is not effective for pristine coals, like the Argonne Premium Coals.
- For the latter coals, an ion-exchange technique in which the coal is first treated by Fe<sup>+3</sup> cations followed by treatment with MoS<sub>4</sub><sup>-2</sup> anions was found to be effective in increasing yields in a two-step liquefaction process (pretreatment at 350 °C, 30 min. followed by liquefaction at 400 °C, 30 min).
- The extent of retrogressive reactions for low rank coals in pyrolysis and liquefaction is significantly reduced by removal of cations exchanged on carboxyl groups, based on experiments where the coal has been ion-exchanged (using NH<sub>4</sub><sup>+</sup>), acid demineralized (using HCl/HF) or methylated.
- The addition of monovalent (K<sup>+</sup>) or bivalent (Ca<sup>+2</sup>, Ba<sup>+2</sup>) cations to acid demineralized coals at pH 8 significantly increases the extent of retrogressive reactions in pyrolysis and liquefaction (liquid yields are reduced). The effect is even more pronounced at pH 12.5.
- The ability of cations to act as initial crosslinks in the coal structure through electrostatic or covalent interactions is believed to be an important aspect of their role in promoting retrogressive reactions.
- Since the moisture in low rank coals is associated with the cations, the presence of liquid water during pyrolysis (as in hydrothermal treatment) or liquefaction can help to mitigate these reactions.
- The benefits of catalytic pretreatment for low rank coals may also be a result of the interaction of the catalyst with the cations present in these coals. It has been reported that alkali metals reduce the effectiveness of Mo catalysts in coal liquefaction (10), suggesting that an interaction does occur.
- The evolution of CO<sub>2</sub> from carboxylate groups appears to be the key indicator of retrogressive reactions in pyrolysis or liquefaction of low rank coals. The removal of the cation, the association of the cation with water or the association of the cation with a highly dispersed catalyst can inhibit the crosslinking events which are normally associated with the decomposition of these groups.

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**Table 1.** Time Resolved Liquid Yields (DAF WT %) from Liquefaction Experiments with Raw and Fe/Mo Exchanged (1.4% Fe/Mo) Argonne Wyodak Coal.

Reaction Time (minutes)	Raw Vac. Dried Coal			1.4% Fe/Mo Exchanged Coal		
	Toluene Solubles			Toluene Solubles		
	Total	Oils	Asphaltenes	Total	Oils	Asphaltenes
0	3	4	7	12	6	6
10				34	12	22
20				48	14	34
30	50	8	42	57	14	43
40				57	15	42
50				62	22	40
90	62	33	29	66	29	37

Notes: Pretreatment done at 350 °C, 30 min.; Liquefaction done at 400 °C, 30 min.; Tetralin/Coal = 6/1

**Table 2.** Results From Characterization of Vac Dry Modified Zap Samples By Programmed Pyrolysis And Solvent Swelling/Pyridine Extraction.

Coal (type/preparation)	Pyrolysis Products (wt.% ,daf)					Solvent Swelling/ Pyridine Extraction	
	Tars	CO <sub>2</sub>	CO	H <sub>2</sub> O	CH <sub>4</sub>	V.S.R. <sup>a</sup>	P <sub>s</sub> <sup>b</sup>
Fresh	7	8.9	14.7	14.3	2.2	2.7	5
Demin.	20	4.8	10.4	8.4	2.7	3.1	20
Demin. + K <sup>+</sup> (pH8)	11	8.6	9.9	16.0	1.9	2.0	10
Demin. + Ca <sup>++</sup> (pH8)	10	8.6	13.5	10.3	2.4	1.8	3
Demin. + Ba <sup>++</sup> (pH8)	6	11.7	15.8	18.6	2.6	2.1	6
Demin. + K <sup>+</sup> (pH12.5)	5	9.9	12.4	13.5	1.6	1.7	2
Demin. + Ca <sup>++</sup> (pH12.5)	4	8.2	22.6	12.6	2.0	1.1	2
Demin. + Ba <sup>++</sup> (pH12.5)	3	10.5	24.1	15.5	2.6	1.1	1

Notes: a = Volumetric Swelling Ratio In Pyridine; b = Pyridine Extractables (daf)

**Table 3.** Liquefaction Results of Vac Dry Modified Zap Samples.

	Toluene Solubles (wt.%, daf)			Gas (wt. %, daf)		
	Total	Oils	Asphaltenes	CO <sub>2</sub>	CO	CH <sub>4</sub>
Fresh	26	12	14	4.3	0.24	0.25
Demin.	52	26	26	1.1	0.43	0.27
Demin. + K <sup>+</sup> (pH8)	30	11	19	7.7	0.27	0.17
Demin. + Ca <sup>++</sup> (pH8)	25	13	12	2.7	0.30	0.22
Demin. + Ba <sup>++</sup> (pH8)	37	25	12	7.3	0.40	0.20
Demin. + K <sup>+</sup> (pH12.5)	17	5	12	5.0	0.24	0.27
Demin. + Ca <sup>++</sup> (pH12.5)	*	*	3	0.7	0.04	0.08
Demin. + Ba <sup>++</sup> (pH12.5)	15	15	0.5	0.3	0.27	0.02

\* Yields Calculated by Difference were Negative. Solvent Incorporation is Suspected.

**Table 4.** Effect of Added Water on Liquefaction of Raw and Demineralized Argonne Zap Coal.

Temp. Level (°C)	Water Addition	Toluene Solubles wt.%, daf		CO <sub>2</sub> Yields wt. %, daf	
		Raw	Demin.	Raw	Demin.
350	yes	13	0	0.0	1.1
	no	1	27	5.4	2.4
375	yes	23	19	2.4	1.5
	no	11	40	5.2	2.2
400	yes	31	24	5.2	0.8
	no	30	58	4.1	4.2

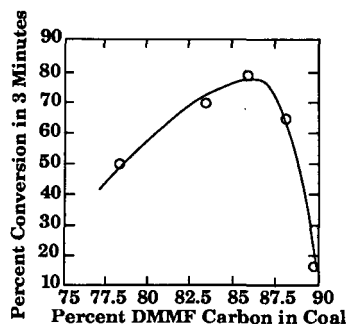


Figure 1. Rank Dependence of Short Contact Time Liquefaction Yields (3).

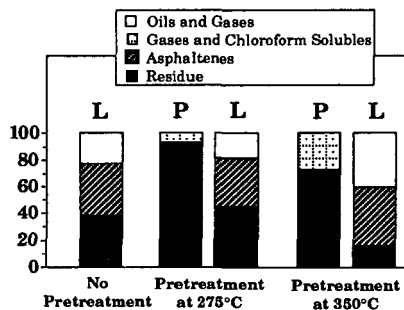


Figure 2. Product Distributions for Preliquefaction and Liquefaction Comparing Results for No Preliquefaction, Preliquefaction at 275°C and Preliquefaction at 350°C. P = Preliquefaction; L = Liquefaction. Liquefaction Conditions - 425°C, Mo, Catalyst, Naphthalene Solvent, Hydrogen Atmosphere (10 min). Preliquefaction Conditions - Mo, Catalyst, Naphthalene Solvent, Hydrogen Atmosphere (275°C-30 min., 350°C - 60 min.).

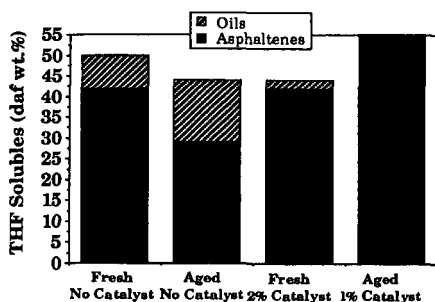


Figure 3. Effect of Coal Aging and Molybdenum Catalyst Impregnation on THF Solubles Yields from Liquefaction of Argonne Wyodak Coal in Tetralin (Pretreatment done at 350°C, 30 min; Liquefaction done at 400°C, 30 min).

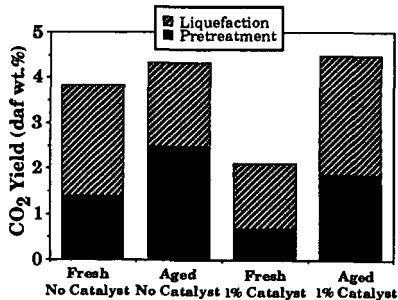
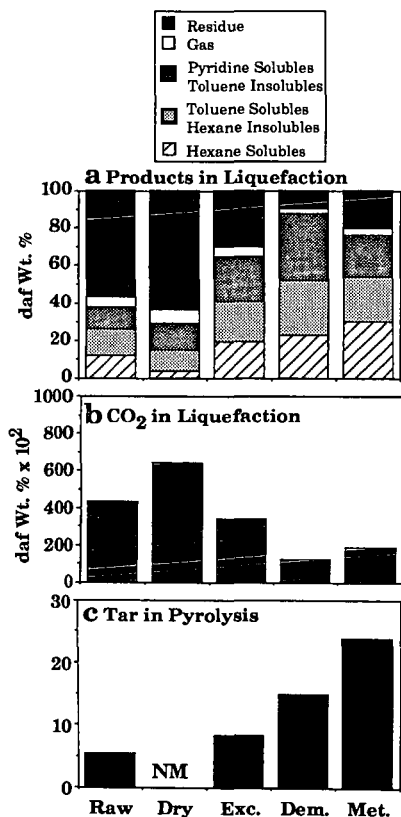
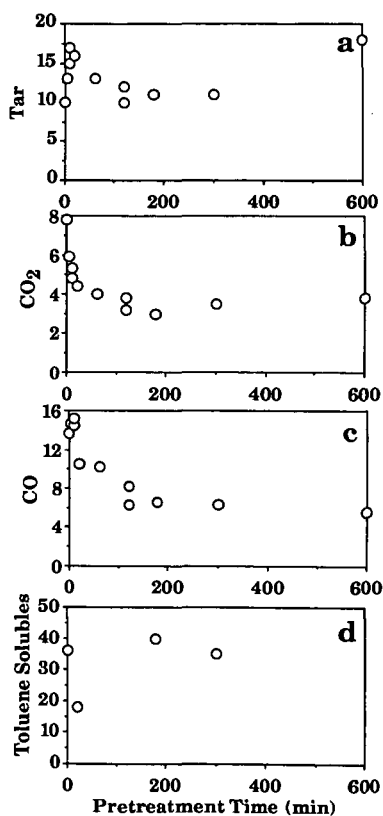


Figure 4. Effect of Coal Aging and Molybdenum Catalyst Impregnation on Total CO<sub>2</sub> Evolution from Pretreatment (350°C, 30 min) and Liquefaction (400°C, 30 min) of Argonne Wyodak Coal.



**Figure 5.** The Variation in Product Distributions for Zap Lignite with Coal Treatment. a) Products in Liquefaction, b) CO<sub>2</sub> in Liquefaction and c) Tar in Pyrolysis. NM = Not Measured.



**Figure 6.** Results from Analysis of Zap Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-c) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (d) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis.

## Enhancing Low-Severity Catalytic Liquefaction of Low-Rank Coal by Adding Water

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**Keywords:** Coal, Liquefaction, Dispersed MoS<sub>2</sub> catalyst, Water addition, Low-rank coal

### INTRODUCTION

As a part of an on-going program for investigating the effects of thermal and catalytic pretreatments on coal structure and reactivity in liquefaction, the present study seeks to explore the effects of water in low-severity catalytic liquefaction of low-rank coal. The motivation of the present study comes from our recent work on the influence of mild pretreatments, drying and oxidation, of Wyodak subbituminous coal on its catalytic liquefaction [Saini et al., 1993; Song et al., 1993]. In that work we found that adding a small amount of water equivalent to the original moisture content (28.4 wt%) back to the vacuum-dried or air-dried coal restored over 90 % of the conversion of the fresh raw coal in non-catalytic runs at 350 °C with and without solvents. This fact strongly suggests that the negative impact of drying on thermal (uncatalyzed) liquefaction reactions is largely due to the removal of water. Another fact that puzzled us is that the conversions of fresh raw coal in the non-catalytic runs and catalytic runs with either tetralin or 1-methylnaphthalene (1-MN) solvent are very similar to each other, although the catalytic runs of the vacuum-dried or air-dried coal afforded significantly higher conversions than the corresponding thermal runs. These two facts prompted us to examine the effects of water addition in catalytic coal liquefaction. This paper reports on the dramatic improvement of coal conversion upon addition of a small amount of water in low-severity liquefaction of Wyodak subbituminous coal using a dispersed molybdenum sulfide catalyst at 350 °C for 30 min.

### EXPERIMENTAL

The coal used was a Wyodak subbituminous coal, which is one of the Department of Energy Coal Samples (DECS-8) maintained in the DOE/Penn State Sample Bank. It was collected in June 1990, ground to  $\leq 60$  mesh, and stored under argon atmosphere in heat-sealed, argon-filled laminated foil bags consisting of three layers. It contains 32.4 % volatile matter, 29.3 % fixed carbon, 9.9 % ash and 28.4 % moisture, on as-received basis; 75.8 % C, 5.2 % H, 1.0 % N, 0.5 % S and 17.5 % O, on dmmf basis. The as-received fresh sample is designated as raw coal. Vacuum-drying (VD) of the coal was conducted in a vacuum oven at 100 °C for 2 h. Air-drying (AD) was done in an oven maintained at 100 °C for 2-100 h, or at 150 °C for 20 h, with the door partially open. For the loading of dispersed catalyst, ammonium tetrathiomolybdate (ATTM) was used as precursor, which is expected to generate molybdenum sulfide particles on coal surface upon thermal decomposition at  $\geq 325$  °C. ATTM was dispersed on to coal (1 wt% Mo on dmmf basis) by incipient wetness impregnation from its aqueous solution. The impregnated coal samples were dried in a vacuum oven at 100 °C for 2 h.

The liquefaction was carried out at 350 or 400 °C for 30 minutes (plus 3 minutes heat-up time) with an initial (cold) H<sub>2</sub> pressure of 7 MPa (1000 psi) in 25 ml tubing bomb microreactor. We conducted three types of reactions including solvent-free runs, the runs in the presence of a hydrogen donor tetralin solvent, and the runs with a non-donor 1-methylnaphthalene solvent, using 4 g of coal and 4 g of solvent, and optionally, added water. The wt ratio of added water to dmmf coal was kept constant (0.46) for both thermal and catalytic runs with added water. After the reaction, the gaseous products were analyzed by GC, with the aid of gas standards for quantitative calibration of GC responses of CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbon gases. The liquid and solid products were separated by sequential Soxhlet extraction into oil (hexane soluble), asphaltene (toluene soluble but hexane insoluble), preasphaltene (THF soluble but toluene insoluble), and residue (THF insoluble). The conversions of coal into soluble products were determined from the amount of THF-insoluble residues. More experimental details may be found elsewhere [Song and Schobert, 1992; Saini et al., 1993]. In order to obtain highly reliable data, almost all the experiments were duplicated or triplicated. The deviations in conversions and product yields are generally within  $\pm 2$  wt%. Most results reported here are average of two runs.

### RESULTS AND DISCUSSION

Tables 1, 2 and 3 show the results for liquefaction of the coal at 350 °C with and without added water in the absence of any solvent (Table 1) and in the presence of a non-donor 1-methylnaphthalene (1-MN) solvent (Table 2) and a hydrogen-donor tetralin solvent (Table 3). Tables 4 and 5 show the results for thermal (non-catalytic) and catalytic runs, respectively, at

higher temperature (400 °C) with and without added water. The data include coal conversion, total yields of gaseous products by two different methods, yields of CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbon gases determined by GC, yields of oil, asphaltene, and preasphaltene obtained from Soxhlet extraction, consumption of gas-phase H<sub>2</sub>, and net hydrogen transfer from solvent where appropriate. These results are grouped and discussed below.

#### **Effect of Water Reflected by the Influence of Drying**

For the thermal (non-catalytic) runs, both vacuum-drying and air-drying decreased coal conversion significantly, as compared to the run of the raw coal. Original fresh raw coal contains 28.4 wt% water. To see whether the changes caused by the drying is reversible or irreversible, we added a small amount of water equivalent to the original moisture content, to the dried coal. The liquefaction results showed that adding water back to the vacuum-dried and air-dried coals restored over 90% of the conversion of the fresh raw coal. The coal conversion levels always follow the order of solvent-free < 1-methylnaphthalene < tetralin; the use of the raw coal always give the highest conversion. In the absence of water, there were some differences between the vacuum-dried and air-dried coals, with the latter affording higher conversion when a solvent was used. When water is added back, the differences between the two types of dried coals become much smaller.

These trends reveal that the major effect of drying on thermal liquefaction is associated with the effect of water. Under the conditions of vacuum-drying at 100 °C for 2 h, most of the changes caused by drying are reversible, as can be seen by the over 90% restoration of coal conversion. The other effects of drying and oxidation may include the changes in pore structure (Suuberg et al., 1991; Vorres et al., 1992), surface characteristics (Song et al., 1993), and, if oxidation involved, the change in functionality (Saini et al., 1993). These kinds of changes may be irreversible if high severity conditions were used for drying. However, when water is added back, the differences caused by using different drying methods, largely diminish. In other words, decrease in conversion caused by some undesirable changes during drying is largely compensated by the desirable effect of water addition.

The results for uncatalyzed runs in Tables 1 to 3 demonstrate that the presence of water promotes the conversion of the coal, increases oil yields, and significantly enhances the oxygen removal as CO<sub>2</sub>. Adding water also resulted in small but consistent decrease in the yield of CO. This is considered to be due to water gas shift reaction:  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ . However, the increase in CO<sub>2</sub> yield upon H<sub>2</sub>O addition is much more than the decrease in CO on a molar basis, indicating the occurrence of other reactions between water and species in or from coal, which led to substantial increase in CO<sub>2</sub> formation.

#### **Positive Effect of Added Water in Catalytic Liquefaction at 350 °C**

For all the catalytic runs listed in Tables 1 to 3, regardless how the coal was pre-dried or undried, all the ATTM-loaded coals were dried in vacuum at 100 °C for 2 h before use. In the runs testing the effect of water addition, we added a small amount of water (H<sub>2</sub>O/dmmf coal = 0.46, wt ratio). It is clear from Table 2 that adding water to the catalytic reactions at 350 °C dramatically promoted the coal conversion from 29-30 wt% for the vacuum-dried or air-dried coals to 62-63 wt% in the solvent-free runs, and from 43 to 66 wt% for the fresh raw coal. Therefore, the present results demonstrate that dispersed MoS<sub>2</sub> catalyst and a small amount of water can act in concert to strongly promote coal conversion at 350 °C. In fact, the use of ATTM with added water at 350 °C without solvent (Table 1) or with 1-MN solvent (Table 2) resulted in coal conversion level (63-66 dmmf wt%) that is much higher than that (30-38 wt%) from the non-catalytic runs at much higher temperature, 400 °C (Table 4).

For the solvent-free runs, the increased coal conversion upon water addition is mainly manifested by the significant gain in asphaltene and preasphaltene yields (Table 1). In the presence of either a H-donor tetralin solvent or a non-donor 1-MN solvent, the enhanced conversions are largely due to the increase in the yields of preasphaltene and oil, and this trend was most apparent with 1-MN solvent (Table 2).

With respects to the effect of water associated with influence of drying, it also appears that dispersing ATTM on vacuum-dried coal gives higher conversion upon water addition, as compared to loading ATTM on air-dried coal. The extents of increase in conversion due to water addition are also higher with the former than with the latter. These results show that for water-aided catalytic liquefaction at 350 °C, less oxidation of the coal sample can lead to higher conversion.

The use of catalyst generally decreased the yield of CO<sub>2</sub> in the runs of the dried coals without added water. Similar to the thermal runs, adding water to the catalytic runs also decreased the CO yield and significantly enhanced the formation of CO<sub>2</sub>. The increasing extent in CO<sub>2</sub> yield is much higher than the decrease in CO yield, indicating the contribution of the reactions between water and coal species, other than water gas shift reaction, to the increased CO<sub>2</sub> formation.

#### **Negative Effect of Added Water in Catalytic Liquefaction at 400 °C**

In order to examine the effect of added water in relation to the influence of reaction temperature, we also carried out the liquefaction experiments at 400 °C. In uncatalyzed runs, adding water resulted in moderate increase in oil yields and coal conversion (5-7 wt%) with 1-MN solvent and without solvent, and small increase in coal conversion with tetralin

solvent. The changes in coal conversion with solvents are much larger at 400 °C than at 350 °C, but conversion always increases in the consistent order of none < 1-MN < tetralin.

As can be seen by comparing Table 5 with Table 4, the trends for the water effect in catalytic runs at 400 °C are different from those in non-catalytic runs. In the absence of added water, the solvent-free run of the vacuum-dried and ATTM-impregnated coal afforded highest conversion, 85 wt%, and highest oil yield, 46 wt%. The run with 1-MN solvent gave the lowest conversion, 71 wt%. Relative to the solvent-free run, the use of H-donor tetralin solvent at 400 °C did not display any advantage in terms of coal conversion and oil yields. Given the fact that water acts as a very good promotor for coal conversion at 350 °C (Tables 1-3), it is surprising to note from Table 5 that adding water to the catalytic runs at 400 °C decreased coal conversion substantially in the runs with 1-MN and without solvent. We conducted duplicated runs under the three different conditions at 400 °C, and confirmed a reproducible trend for the negative impact of water on the catalytic reactions at 400 °C. The solvent-free run suffered large decrease in coal conversion from 85 to 62 wt%. The run with tetralin displayed less sensitivity to the water, with slight but consistent decrease in conversion in duplicated runs from about 84 to 80 wt%.

These results show that the catalytic activity is significantly lower in the presence of water at 400 °C, indicating that water is detrimental for liquefaction at higher temperature. The action of water at 400 °C may be inferred through the following comparative examination. The highest oil yield and the highest conversion in the solvent-free run with no added water indicate that dispersed molybdenum catalyst exhibited maximum activity in activating molecular H<sub>2</sub>, namely dissociation of H<sub>2</sub> on catalyst surface, and in transfer of the active H atom to the coal-derived free radicals and other coal species when there is no externally added solvent. Relative to the solvent-free catalytic run, the decrease in conversion and H<sub>2</sub> consumption upon addition of 1-MN may be attributed to the decrease in partial H<sub>2</sub> pressure, additional difficulty in mass transport of H<sub>2</sub> to the catalyst surface in the presence of solvent, and competitive adsorption of aromatic 1-MN molecules on catalyst surface. The same trends also applies to the run using tetralin, but the negative impact of tetralin to mass transport of H<sub>2</sub> gas is largely compensated by hydrogen donation from benzylic hydrogens in tetralin. As a result, oil yield decreased but conversion did not decrease as much as oil yield. Relative to the runs with added 1-MN, the added water initially occupied less space and therefore the partial H<sub>2</sub> pressure should be higher during the water-added but solvent-free run. Such a inference indicates that the presence of water deactivated the catalyst. The conversion decrease due to water addition was also accompanied by significant reduction in gas-phase H<sub>2</sub> consumption, from 2.8 to 1.4 in solvent-free runs, and from 1.8 to 0.7-0.9 in the runs with a solvent (Table 5). It should also be noted that the enhanced formation of CO<sub>2</sub> upon water addition seems to be unaffected at higher temperature, suggesting the enhanced CO<sub>2</sub> formation is caused by thermal reaction between added water and coal species.

#### The Desirable and Undesirable Functions of Water at 350 and 400 °C

Little is reported in literature about the effects of water on the catalytic coal liquefaction using dispersed catalyst. However, for non-catalytic coal conversion such as pyrolysis, liquefaction and coprocessing, hydrothermal pretreatments of coal has been reported to be beneficial in terms of increased conversion, or oil yield (Graff and Brandes, 1987; Bienkowski et al., 1987; Ross and Hirschon, 1990; Pollack et al., 1991; Serio et al., 1991; Tse et al., 1991). Siskin et al. (1991) have suggested that the presence of water during coal pretreatment will facilitate depolymerization of the macromolecular structure to give an increased proportion of liquids by cleaving important thermally stable covalent crosslinks in the coal structure. On the other hand, Tse et al. (1991) suggested that the pretreatments of low rank coals in the presence of water should minimize retrogressive reactions such as crosslink formation by phenolic compounds such as catechol and lead to higher conversion or a better quality product. The present results for thermal runs are consistent with those in literature. However, there is no comparable literature data for the desirable and undesirable effects of water addition in catalytic liquefaction. Ruether et al. (1987) reported that in uncatalyzed systems, a substantial water partial pressure at fixed H<sub>2</sub> partial pressure increases the conversion of Illinois #6 bituminous coal, but in the runs using 0.1% dispersed Mo catalyst at 427 °C for 60 min, highest conversions are obtained without added water. How water affects the catalytic reaction is not clear. The present results suggest that water promotes coal liquefaction with dispersed MoS<sub>2</sub> catalyst at 350 °C (Tables 1 to 3), but has less promoting effect to thermal reaction at 400 °C (Table 4) and can deactivate or passivate the catalyst at 400 °C (Table 5).

#### CONCLUSIONS

Water can be excellent promotor or undesirable inhibitor for coal conversion in catalytic liquefaction, depending on the reaction systems and conditions. For catalytic liquefaction at 350°C, adding a small amount of water has a dramatic promoting effect on coal conversion, but a significant inhibiting effect of water is observed for catalytic runs at 400 °C. It appears that water and dispersed molybdenum sulfide catalyst can act in concert to promote coal conversion and oil production at 350 °C, but water can passivate the catalyst at 400°C. The remarkably high conversion level at low-temperature (350 °C) achieved with the co-use of ATTM and added water may give rise to new opportunities for developing novel low-severity catalytic liquefaction processes with significantly reduced operational costs.

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Table 1. Effects of Water Addition on Solvent-Free Liquefaction of DECS-8 Wyodak Coal at 350 °C for 30 min under 6.9 MPa H<sub>2</sub>

ID No.	51/63/93	7	2632	90/139	119	54/66/96	10	29/55	116	113	122/42	
Coal Sample <sup>a</sup>	Raw		VD-100°C-2 h		AD-100°C-2 h		VD-100°C-2 h		AD-100°C-2 h		AD-100°C-2 h	
	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free	Solvent-free
Catalyst (ATTM)	-		-		-		ATTM		ATTM		ATTM	
	Original H <sub>2</sub> O	-	-	-	H <sub>2</sub> O added	-	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added
Prod. dmuf wt%												
Conversion	25.0	12.5	14.8	22.5	26.1	43.3	29.8	29.2	66.0	66.5	62.3	62.3
Gases	7.7 <sup>b</sup> (9.52) <sup>c</sup>	3.3 (4.93)	5.0 (6.33)	7.4 (8.64)	8.4 (11.49)	2.2 (4.11)	3.0 (2.78)	3.3 (6.20)	6.2 (8.41)	6.5 (9.20)	6.6 (7.50)	6.6 (7.50)
CO	0.37	0.24	0.26	0.12	0.17	0.24	0.19	0.38	0.04	0.04	0.03	0.03
CO <sub>2</sub>	8.90	4.50	5.93	8.27	11.11	3.52	2.30	5.18	8.18	8.70	7.09	7.09
C <sub>1</sub> -C <sub>4</sub>	0.25	0.19	0.14	0.25	0.21	0.35	0.29	0.59	0.44	0.46	0.38	0.38
Oil	5.4 (3.1) <sup>d</sup>	2.1	3.3	5.4 (3.1)	8.5	16.9	10.0	12.6	13.0	13.3	13.4	13.4
Asphaltene	2.8	2.6	0.7	2.3	2.1	9.2	5.4	3.2	19.9	21.6	19.5	19.5
Preasphaltene	9.1	4.5	5.8	7.6	7.1	14.9	11.4	10.1	26.9	25.1	22.9	22.9
H <sub>2</sub> consum, dmuf wt%												
H <sub>2</sub> gas	0.72	0.20	0.28	0.44	0.43	1.92	1.35	1.34	1.64	1.70	1.73	1.73
H <sub>2</sub> -donor sol												

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD). b) The gas yields determined by weighing the microreactor before reaction and after releasing the gaseous products. c) The figures in parentheses are the gas yields determined by GC and volumetric analyses. d) Yield of physically recovered oil.

Table 2. Effects of Water Addition on Liquefaction of DECS-8 Wyodak Coal at 350 °C for 30 min in 1-Methylnaphthalene under 6.9 MPa H<sub>2</sub>

ID No.	53/65/95	9	28/74	92/141	121	56/68/98	12	31/37	118	115	124/144
Coal Sample <sup>a</sup>	Raw	VD-100°C-2 h	AD-100°C-2 h	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h
Solvent	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN	1-MN
Catalyst (ATTM)	-	-	-	-	-	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM
H <sub>2</sub> O Added	Original H <sub>2</sub> O	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	-	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added
Prod. dmuf wt%											
Conversion	38.4	18.3	22.7	34.8	36.5	35.9	31.1	37.4	60.0	56.0	51.7
Gas	6.4 <sup>b</sup> (7.34) <sup>c</sup>	4.0 (4.66)	5.1 (6.58)	6.4 (7.14)	8.9 (10.93)	3.2 (4.96)	2.6 (3.7)	3.0 (5.8)	5.7 (9.82)	5.8 (10.39)	6.8 ( )
CO	0.14	0.16	0.25	0.11	0.16	0.14	0.11	0.19	0.04	0.05	0.04
CO <sub>2</sub>	7.02	4.34	6.18	6.84	10.57	4.48	3.37	5.23	9.46	9.99	8.54
C <sub>1</sub> -C <sub>4</sub>	0.18	0.16	0.15	0.19	0.20	0.34	0.25	0.37	0.32	0.35	0.28
Oil	15.9	1.1	4.2	11.2	12.2	10.4	6.1	10.3	25.3	15.4	15.5
Araphene	6.6	5.8	4.0	7.1	6.9	10.4	10.1	8.1	9.6	13.2	9.5
Phenanthrene	11.4	7.4	9.4	10.1	8.4	11.9	12.3	16.0	19.5	21.6	19.9
H conum, dmuf wt%											
H <sub>2</sub> gas	0.58	0.45	0.43	0.44	0.29	1.17	1.00	1.08	0.99	1.02	0.75

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD). b) The gas yields determined by weighing the microreactor before reaction and after releasing the gaseous products. c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses.

Table 3. Effects of Water Addition on Liquefaction of DECS-8 Wyodak Coal at 350 °C for 30 min in Tetralin under 6.9 MPa H<sub>2</sub>

ID No.	52/6494	8	27/93/93a	91/140	120	55/67/97	11	30/36	117	114	123/143
Coal Sample <sup>a</sup>	Raw	VD-100°C-2 h	AD-100°C-2 h	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h	Raw	VD-100°C-2 h	AD-100°C-2 h
Solvent	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin	Tetralin
Catalyst (ATM)	-	-	-	-	-	ATM	ATM	ATM	ATM	ATM	ATM
H <sub>2</sub> O Addition	Original H <sub>2</sub> O	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	-	-	-	H <sub>2</sub> O added	H <sub>2</sub> O added	H <sub>2</sub> O added
Prod. dmmt wt%											
Conversion	43.3	25.9	35.1	40.0	40.4	42.2	36.4	45.6	64.1	62.9	60.5
Gas	5.8 (7.71) <sup>c</sup>	4.2 (4.4)	5.4 (6.3)	6.0 (7.31)	7.1 (9.60)	2.8 (4.94)	3.0 (2.9)	3.9 (5.47)	5.9 (9.67)	6.2 (8.96)	5.7 (8.10)
CO	0.11	0.19	0.24	0.10	0.19	0.14	0.13	0.21	0.05	0.04	0.03
CO <sub>2</sub>	7.41	4.10	5.91	7.01	9.20	4.45	2.58	4.83	9.27	8.57	7.79
C <sub>1</sub> -C <sub>4</sub>	0.19	0.15	0.19	0.20	0.21	0.35	0.28	0.43	0.35	0.35	0.28
Oil	15.8	4.1	11.7	14.0	16.6	16.0	10.2	15.7	18.2	20.8	18.1
Asphaltene	9.3	7.6	7.4	10.5	5.9	11.5	12.9	11.1	13.9	13.8	9.3
Preasphaltene	12.4	10.0	10.6	7.9	10.8	11.9	10.6	14.9	26.1	22.0	27.4
H <sub>2</sub> consum, dmmt wt%											
H <sub>2</sub> gas	0.67	0.29	0.24	0.48	0.19	1.21	1.35	1.36	1.07	1.37	0.81
H <sub>2</sub> -donor sol	0.28	0.41	0.47	0.36	0.42	0.24	0.08	0.14	0.28	0.22	0.26

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD). b) The gas yields determined by weighing the microreactor before reaction and after releasing the gaseous products. c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses.

Table 4. Effect of Water Addition on Thermal Liquefaction of DECS-9 Coal at 400 °C

ID No.	73	133/162	60	135/164	59/87	134/163
Coal Sample <sup>a</sup>	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h
Solvent	Solvent-free	Solvent-free	1-MN	1-MN	Tetralin	Tetralin
Catalyst (ATTM)	—	—	—	—	—	—
H <sub>2</sub> O Addition	—	H <sub>2</sub> O added	—	H <sub>2</sub> O added	—	H <sub>2</sub> O added
Prod. dmmf wt%						
Conversion <sup>b</sup>	30.3	35.4	38.2	43.1	71.4	73.1
Gas	8.8 <sup>b</sup> (7.6) <sup>c</sup>	12.3 (12.54)	8.5 (9.78)	10.3 (12.45)	8.4 (9.37)	10.3 (12.39)
CO	0.41	0.21	0.25	0.25	0.33	0.25
CO <sub>2</sub>	6.35	11.26	8.56	10.75	7.80	10.55
C <sub>1</sub> -C <sub>4</sub>	0.85	1.07	0.97	1.45	1.24	1.59
Oil	10.4 (5.3) <sup>d</sup>	16.1	13.1	20.7	27.3	32.0
Asphaltene	1.8	2.2	7.4	6.1	16.4	16.3
Preasphaltene	10.5	4.8	9.2	6.0	19.3	14.4

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD).

b) The gas yields determined by weighing the microreactor before reaction and after releasing the gases.

c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses. d) Recovered oil.

Table 5. Effect of Water Addition on Catalytic Liquefaction of DECS-9 Coal at 400 °C

ID No.	148/155	136/165	150/157	138/167	149/156	137/166
Coal Sample <sup>a</sup>	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h	VD-100 °C-2h
Solvent	Solvent-free	Solvent-free	1-MN	1-MN	Tetralin	Tetralin
Catalyst (ATTM)	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM
H <sub>2</sub> O Addition	—	H <sub>2</sub> O added	—	H <sub>2</sub> O added	—	H <sub>2</sub> O added
Prod. dmmf wt%						
Conversion	85.4	62.1	70.9	61.8	83.6	80.3
Gas	7.5 <sup>b</sup> (10.1) <sup>c</sup>	11.4 (11.23)	7.3 (9.91)	9.7 (12.82)	7.7 (9.74)	9.7 (12.73)
CO	0.10	0.02	0.18	0.02	0.17	0.03
CO <sub>2</sub>	7.39	9.57	7.87	11.31	7.71	11.14
C <sub>1</sub> -C <sub>4</sub>	2.61	1.64	1.86	1.49	1.86	1.56
Oil	45.8	28.2	34.0	28.1	36.4	34.0
Asphaltene	19.7	10.5	12.8	10.7	16.9	14.9
Preasphaltene	12.4	12.0	16.9	13.3	22.6	21.7
H <sub>2</sub> consum. dmmf wt%						
H <sub>2</sub> gas	2.80	1.38	1.81	0.90	1.75	0.72

a) Including fresh raw coal (Raw); vacuum-dried at 100°C for 2 h (VD); air-dried at 100°C for 2 h (AD).

b) The gas yields determined by weighing the microreactor before reaction and after releasing the gases.

c) The figures in parenthesis are the gas yields determined by GC and volumetric analyses.

## SOLVENT AND PRETREATMENT EFFECTS ON COAL SWELLING

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Keywords: Coal, solvent swelling.

### ABSTRACT

Swelling ratios were determined with a wide variety of solvents and solvent blends using pulverized samples of Black Thunder, (WY) subbituminous, Burning Star (IL) bituminous, and Martin Lake (TX) lignite. Experiments were also conducted with 8 x 60 mesh raw and sulfurous acid-treated Black Thunder coal. Only marginal levels of swelling were observed for the hydrocarbon solvents, while hetero-functional solvents enhanced swelling ratios. Oxygenates gave equilibrium swelling ratios,  $Q$ , in the range of 1.15 to 1.6, with tetrahydrofuran as the most effective. Selected nitrogen-containing solvents and dimethyl disulfide were also effective, with  $Q$  ratios ranging from 1.6 to 2.7. As a result of sulfurous acid-treatment to remove the alkali and alkaline earth ions, the swelling of Black Thunder coal was enhanced. The effects of coal type may be attributed to the interaction of the solvent with the bonds present in both the raw and acid-treated coals. Experiments with blends of effective and non-effective solvents gave much greater  $Q$  ratios than those expected from an linear combination of the two solvents. The greatest synergisms were observed with Black Thunder and Burning Star coals.

### INTRODUCTION

Van Krevelen<sup>(1)</sup> proposed that coals are three-dimensionally cross-linked macromolecular networks. The area was expanded upon.<sup>(2-5)</sup> When brought into contact with most organic solvents, coals absorb the solvent and swell. The two factors which control the amount of swelling are the magnitude of the solvent-coal interactions and the cross-link density of the coal. Another aspect is that coals can behave as either a glass or rubber with a transition zone. In a glassy state, the macromolecular chains are constrained and diffusion through the coal matrix is quite slow. In the rubbery state, the macromolecular chains can move relatively freely, and diffusion rates in the solid approach those in liquids. Some solvents can cause a glass-to-rubber transition to occur in coals.

Coal swelling solvents can be divided into two classes: non-hydrogen bonding and hydrogen bonding. The swelling ratios of the coal samples in non-hydrogen bonding solvents are significantly less than those in hydrogen bonding solvents. The most effective solvents are those containing a nitrogen or oxygen atom possessing an unshared pair of electrons. The strong hydrogen bonding solvents replace the coal-coal hydrogen bonds with new coal-solvent hydrogen bonds. If the coal-coal hydrogen bonds are active cross-links, the replacement would result in a lower cross-link density which would cause swelling to increase. The weak hydrogen bonding solvents result in less swelling since more coal-coal hydrogen bonds remain intact.

### EXPERIMENTAL

Coal swelling experiments were made using (1) Martin Lake lignite, (2) Black Thunder subbituminous, and (3) Illinois No. 6 bituminous coals. The coals were dried and handled in nitrogen whenever possible. The coals were either

sieved and ground to -325 mesh under nitrogen, or used as coarse (8 x 60 mesh) material. Samples of raw and SO<sub>2</sub>-treated Black Thunder coal, that were partially dried to 8 wt% moisture content at ambient temperature in nitrogen, were also used.

The experimental procedure for the first set of samples consisted of placing samples of dry coal in a 1 mm. o.d. tube followed by centrifuging for 60 minutes. The height of the coal was measured as  $h_1$ . After breaking up the column of packed coal, solvent in excess was introduced and the tube was vigorously shaken to ensure thorough mixing. The slurry was centrifuged after specified times and the height was measured as  $h_2$ . The swelling ratio was defined as the ratio of the resulting heights of swelled and raw coal ( $Q = h_2/h_1$ ). In the experiments with the coarse coal samples, 10 ml conical centrifuge tubes were used.

## RESULTS AND DISCUSSION

**Reproducibility:** Experiments were made to determine reproducibility using two technicians to make multiple parallel tests. Reproducibility was good. At low swelling ratios, such as those of the methanol runs (average  $Q$  of 1.28), the standard deviation averaged about  $\pm 0.06$ . At high swelling ratios (tetrabutyl ammonium hydroxide,  $Q$  averaging about 2.5), the standard deviation averaged about  $\pm 0.14$ .

**Effect of Solvent Type and the Interaction with Coal Pretreatment:** The results of swelling ratio experiments using finely pulverized (through 325 mesh) coal samples are given in Table I. Only marginal levels of coal swelling were observed for the hydrocarbon solvents including hexane, cyclohexane, single-ring aromatics, and tetralin.

Swelling greatly increased with the introduction of hetero-functionality. Equilibrium (96 hour contact) swelling ratios of the three coals with alcohols and ketones fell in the range of 1.15 to 1.4. There appeared to be no consistent effect of the type (molecular weight) of alcohol or ketone, but the Black Thunder coal swelled to a greater extent than the other coals. Cresol was a more effective swelling agent than the above oxygenates in the case of Illinois No. 6 coal, but it was the same for the other coals. The results with methyl acetate were the same as those of the above oxygenates. Tetrahydrofuran (THF) was a significantly more effective coal swelling solvent than the other oxygenates. The  $Q$  ratios ranged from 1.38 to 1.63.

The nitrogen-containing compounds varied greatly in their effectiveness to swell these coals. The highly polar compound, tetrabutylammonium hydroxide (TBAH), was very effective with a range of  $Q$  ratios of 2.18 to 2.66. Aniline was quite effective for Illinois No. 6 and Black Thunder coals (1.94 and 1.64, respectively), but it was essentially ineffective (1.19) for Martin Lake lignite. Nitrobenzene was poor for all three coals (1.11 to 1.19).

Dimethylsulfoxide was tested due to its unusual solvent properties in other systems. It was found to be particularly effective for the Black Thunder and Illinois No. 6 coals and moderately effective for Martin Lake lignite (2.39, 2.15, and 1.63, respectively).

The results of coal swelling experiments carried out with 8X60 mesh size fractions of both raw and SO<sub>2</sub>-treated Black Thunder coal are given in Table II. There appeared to be little or no effect of coal particle size upon the swelling ratio. However, the SO<sub>2</sub>-treated coal swelling was significantly

greater than that of the raw coal. The removal of alkali and alkaline earth ions from the subbituminous coal reduced the interaction of coal species with each other.

The above differences in swelling are attributed to the interaction of the solvent with the various bonds present in coal. The low rank coals contain significant amounts of ionic and hydrogen bonds due to the presence of a relatively large number of polar functional groups, while the high rank coals contain more charge transfer complexes because of their higher aromatic content. TBAH, which is a very basic solvent, interacts with the ionic and hydrogen bonds readily, thus swelling the Martin Lake lignite to the greatest extent. This is followed by Black Thunder coal and Illinois No. 6. On the other hand, THF disrupts charge transfer complexes, which are predominant in Illinois No. 6, a higher rank coal, thus resulting in a swelling trend opposite to that of TBAH. The increase of swelling ratio in the case of SO<sub>2</sub> treatment is an obvious extension of this theory, especially with the removal of divalent metal ions, such as calcium.

**Effect of Solvent Blends:** The results of experiments made with 325 mesh coal samples and blends of tetralin (TET) and isopropanol (IPA) are shown in Table I and Figure 1. There was a high level of synergism with an advantage of using these blends over the pure solvents. In all cases, the swelling ratios were much greater than those derived from a linear correlation between the pure solvents.

As shown in Figures 2 and 3, the synergism of coal swelling solvents also was demonstrated for methanol/water, dimethyl sulfoxide/tetralin, methanol/tetralin, and isopropanol/water. Experimentation was also carried out with the 8X60 mesh fractions of raw and SO<sub>2</sub>-treated Black Thunder coal, as given in Table II. Again, there were high levels of synergism of solvent blends with both samples of coal.

There is a distinct advantage of using solvent blends to swell coal, because relatively low levels of swelling agent would be needed to be effective in treating coal feed slurries for a liquefaction plant.

#### **CONCLUSIONS**

The following conclusions are drawn from the coal swelling studies:

1. Only marginal levels of coal swelling were observed for the hydrocarbon solvents including paraffins, cycloparaffins, and aromatics.
2. Swelling ratios were greatly increased with the use of solvents having heteroatom functionality.
3. The effectiveness of the oxygenates increased in the following order: alcohols, ketones, methyl acetate < cresol < tetrahydrofuran.
4. The swelling ratios generated by nitrogen-containing compounds increased as follows: nitrobenzene < aniline < tetrabutylammonium hydroxide.
5. High coal swelling ratios were observed with dimethylsulfoxide.
6. Solvent synergism was observed in that the swelling ratios of solvent blends were much greater than those derived from a linear correlation between the pure solvents.

#### **ACKNOWLEDGMENT**

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Table I  
SWELLING RATIO OF COAL/SOLVENT BLENDS  
(325 Mesh Coal with 1 ml Winthrobe Tubes)

Solvent/Time	Black Thunder		Illinois No. 6		Martin Lake Lignite	
	24 Hr	96 Hr	24 Hr	96 Hr	24 Hr	96 Hr
Hexane	--	1.01	--	1.00	--	0.95
Cyclohexane	--	1.00	1.00	1.00	--	--
Benzene	--	1.12	--	1.06	--	1.14
Toluene	--	1.04	--	1.16	--	1.00
Xylene	--	1.02	--	1.04	--	1.05
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Methanol	1.28	1.33	1.16	1.23	1.43	1.36
Ethanol	--	1.31	--	1.26	--	1.24
Isopropanol	1.30	1.39	1.06	1.13	1.14	1.25
Isopropanol	1.30	1.39	1.06	1.13	1.14	1.25
33% Tetralin/67% IPA	1.40	1.53	1.31	1.43	1.18	1.37
67% Tetralin/33% IPA	1.39	1.47	1.34	1.49	1.18	1.36
80% Tetralin/20% IPA	1.34	1.42	1.22	1.35	1.10	1.23
90% Tetralin/10% IPA	1.22	1.33	1.13	1.19	1.10	1.18
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Cresol	1.16	1.29	1.28	1.48	1.13	1.20
Acetone	--	1.32	--	1.24	--	1.25
Methyl Ethyl Ketone	1.32	1.34	1.29	1.29	1.27	1.3
Methyl Acetate	1.28	1.34	1.20	1.20	1.23	1.25
Tetrahydrofuran	1.43	1.53	1.30	1.63	1.36	1.38
Chloroform	--	1.17	--	1.19	--	1.03
Chlorobenzene	1.08	1.08	1.07	1.16	1.09	1.12
Nitrobenzene	1.11	1.15	1.18	1.19	1.08	1.11
Aniline	1.41	1.64	1.71	1.94	1.12	1.19
Tetrabutylammonium Hydroxide	2.05	2.45	1.59	2.18	2.04	2.66
Dimethyl Sulfoxide	2.19	2.39	2.08	2.15	1.52	1.63

Table II

SWELLING RATIO OF THREE SAMPLES OF BLACK THUNDER COAL  
(10 ml Conical Centrifuge Tubes)

Solvent/Time	Untreated -325 Mesh				Untreated 8 $\mu$ 60 Mesh				SO <sub>2</sub> -Treated 8 $\mu$ 60 Mesh			
	2 Hr	4 Hr	24 Hr	96 Hr	2 Hr	4 Hr	24 Hr	96 Hr	2 Hr	4 Hr	24 Hr	96 Hr
Isopropanol	--	--	--	--	1.20	--	1.25	--	1.27	--	1.42	--
501 IPA/501 H <sub>2</sub> O	--	--	--	1.38	--	--	--	--	--	--	1.40	1.40
201 IPA/801 Tetralin	1.16	--	1.24	--	1.25	--	1.48	--	1.33	1.38	1.41	1.41
201 IPA/801 Toluene	--	--	--	--	1.18	--	1.21	--	1.26	--	1.42	--
301 IPA/701 Toluene	--	--	--	--	1.20	--	1.24	--	1.38	--	1.51	--
401 IPA/601 Toluene	--	--	--	--	1.18	--	1.30	--	1.32	--	1.36	--
Methanol	1.34	1.43	1.43	--	--	--	1.26	1.26	1.24	--	--	--
(repeat)	--	--	1.33	--	--	--	--	--	1.18	--	--	--
701 MeOH/301 H <sub>2</sub> O	--	--	1.32	--	1.24	--	1.24	--	--	--	1.25	--
501 MeOH/501 H <sub>2</sub> O	--	--	1.36	--	--	--	--	--	--	--	1.21	--
301 MeOH/701 H <sub>2</sub> O	--	--	1.21	1.28	--	--	--	--	--	--	--	--
251 MeOH/751 Tetralin	1.43	1.46	1.49	--	--	--	--	--	--	--	--	--
Acetone	--	--	--	--	1.23	--	1.24	--	1.52	--	1.52	--
Tetrahydrofuran	--	--	1.42	1.55	--	--	1.54	1.59	--	1.94	--	2.08
701 THF/301 H <sub>2</sub> O	--	--	1.87	1.91	1.71	--	1.86	--	1.93	--	2.15	--
501 THF/501 H <sub>2</sub> O	--	--	1.78	1.85	--	--	--	--	--	--	--	--
301 THF/701 H <sub>2</sub> O	--	--	1.52	1.60	1.36	--	1.49	--	1.43	--	1.52	--
201 THF/801 H <sub>2</sub> O	1.40	1.46	1.46	--	--	--	--	--	--	--	--	--
101 THF/901 H <sub>2</sub> O	1.24	1.24	1.31	--	--	--	--	--	--	--	--	--
51 THF/951 H <sub>2</sub> O	1.40	1.38	1.41	--	1.14	--	1.16	--	1.16	--	1.16	--
(repeat)	--	--	--	--	--	--	--	--	1.17	--	1.15	--
Aniline	--	--	--	--	1.17	--	1.37	--	1.22	--	1.68	--
(repeat)	--	--	--	--	--	--	--	--	1.21	--	1.97	--
Dimethyl Sulfoxide	2.05	2.37	2.37	2.37	1.60	--	2.09	--	2.28	2.35	2.41	2.56
101 DMSO/901 Tetralin	1.39	1.49	1.58	--	1.21	--	1.60	--	--	--	1.83	--
51 DMSO/951 Tetralin	1.19	1.27	1.32	--	1.13	--	1.43	--	1.23	--	1.44	--

Figure 1  
Swelling Ratios of 325-mesh Coal with the IPA/Tetralin System

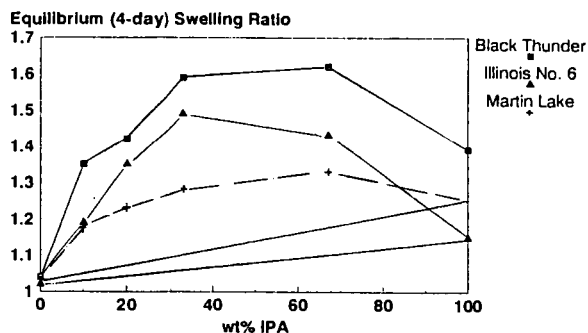


Figure 2  
Swelling Ratios of 325-mesh Black Thunder Coal with the THF/Water System

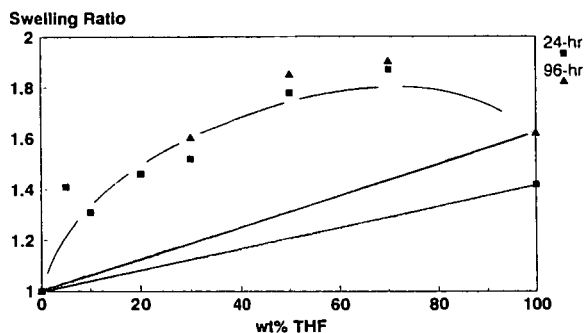
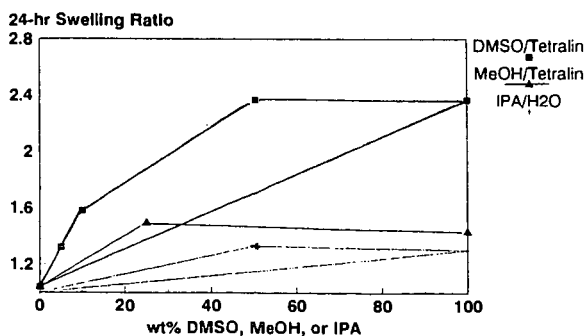


Figure 3  
Swelling Ratios of 325-mesh Black Thunder Coal with Solvent Blends



## ION EXCHANGE PROPERTIES OF WYODAK PREMIUM COAL SAMPLES

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### ABSTRACT:

Low rank coals (lignite and subbituminous) contain exchangeable cations. A sample of -20+200 mesh Argonne Premium Wyodak coal was washed with nitric acid in a burette fitted with a coarse glass frit at the base of the graduations to remove the exchangeable cations from the system. The eluent was passed to a flow-through pH electrode and a titration curve was obtained on a computer file. A series of electrodes (pH, calcium, sodium and potassium) were used in separate experiments to follow the elution from the coal. Some implications for coal structure are also indicated.

### INTRODUCTION:

The abundant reserves of low rank coals in the United States are potentially useful for the production of synthetic liquid fuels. In addition the structure of these coals is becoming better understood but significant additional information is needed to optimize this use.

The coal structure involves polymers of molecules derived from the lignin in the original plants. This structure is known to contain several reactive functional group types including carboxylate and phenolic. The carboxylates are known to be able to act as ion-exchange materials. The functional groups are frequently linked to a variety of alkali and alkaline earth cations. The inorganic cations can be detrimental due to fouling of boilers during operation or reducing yields for liquefaction.

The latter deleterious effects of calcium in the coal (and any other exchangeable cations) can be overcome by removal of these species. A number of studies have indicated that low rank coals can be treated with acids to exchange the cation species with hydrogen ions (1-3). The cations can then be washed away from the coal to minimize their effect.

Cations with a single charge can be attached to a single carboxylate group. Calcium may be present in either or both of two forms. In one case the doubly charged cation can be bound to one hydroxyl and one carboxylate group. This represents a more easily removed form. The second case involves simultaneous bonding to two nearby carboxylate groups. Removal of this calcium involves release from one carboxylate, and later from the second. This process is more difficult and would appear more slowly.

### EXPERIMENTAL:

The coal sample was the Argonne Premium Wyodak subbituminous (4). This coal contains (dry basis) 8.7% mineral matter from low temperature ashing. The 8.7% is made up of: 2.0% quartz, 0.1% pyrite, 0.4% calcite and 6.2 % clays which may be kaolinite (5). The -20 mesh samples were dry screened to -20+200 mesh. Weighed

amounts (about 30 grams) of the screened samples were slurried with deionized water. Fines (still -200 mesh) were decanted away from the slurry using about 200-600 ml of water. The slurry was washed into a special 50 ml burette. The burette had been fitted with a coarse fritted glass disk at the 50 ml mark to retain the coal but allow solutions to pass. Fine coal particles had to be removed to avoid pluggage of the frit. A peristaltic pump provided a uniform flow of 0.1 N  $\text{HNO}_3$  to the sample. Acid flow rates were typically about 1-3 ml/minute and were set according to the ability of the solution to pass through the coal bed. Following the treatment with the acid, the samples were washed with distilled water fed by the peristaltic pump, and the record of pH and ion concentration was obtained in a manner similar to that for the acid treatment. The burette tip was fitted with tubing to connect a flow-through pH electrode from Cole-Parmer, or from Microelectrodes, Inc (Londonderry, NH). For some of the later experiments the pH electrodes were augmented with ion-selective electrodes for  $\text{Ca}^{2+}$ , and  $\text{Na}^+$ . The electrodes were used with an Orion EA940 pH meter. The pH meter in turn was connected to an IBM model AT computer for data acquisition. A schematic diagram of the equipment is given in Figure 1. A program was written which allowed data points to be acquired at specific intervals in the range of 10-18 seconds. The data files were then manipulated with a word processor and Lotus 123 macros to permit plots to be drawn of the data.

The pH electrodes were calibrated with Cole Parmer standard buffers of pH 4 and 7. The ion selective electrodes were calibrated with standard solutions made up of a series of analyzed reagents salts diluted to give 0.1, 0.01 and 0.001 M solutions for each of the cations. Calibrations were checked at the end of the runs.

This arrangement does give a different approach to an endpoint than a simple titration since the exchanged cations are removed from the system.

#### RESULTS AND DISCUSSION:

The results for the Wyodak sample with the pH and sodium electrode are shown in Figure 2. A number of features are evident. The pH changes for the Wyodak coal titrated with 0.1 N nitric acid indicate an initial period in which the water in contact with the coal was displaced by the acid (pH about 6.5 to 5). During this time the soluble species were released and contributed to a near neutral state. This period was followed by an extensive period in which the pH was steady at about 5. During this time the other cations associated with carboxylate groups were exchanging with hydrogen ions and being eluted. At the end of this phase a pair of inflections was exhibited before reaching the pH of the input acid.

The Na electrode indicated that the Na was eluted early in the exchange process, and tailed off slowly. The increase near the end of the acid addition is associated with a change in sensitivity with pH and is not associated with an increase in Na concentration. The most readily released species was released first. The pH remained high after the sodium release indicating that other species were reacting with the acid.

Figure 3 shows the effect of washing the coal with acid and monitoring the calcium ion concentration as well as the pH. A number of features can be seen. The initial pH for this solution is higher than for the sodium, believed to be due to the use of a smaller amount of water to decant the fines, and more of the soluble species were retained in the slurry and eluted in this stage. These species are alkaline as the pH exceeds 7. As the water is displaced from the coal by the acid the pH drops to about 6. During this period an initial calcium species is eluted. There is a slight increase to about pH 6.2 and a long period of very slow decrease to pH 6.1. During this period there is a rapid rise of the calcium concentration (dissolution of calcite is at least partially responsible) and then a slow and consistent increase to a maximum. Just before the maximum calcium concentration the pH drops from about 6.1 to about 4. During this period there is a rapid decrease in the calcium concentration. This is followed by an even more rapid decrease in pH to about 1.15, accompanied by a very rapid decrease in the calcium ion concentration. An instrumental problem caused the discontinuity in the pH curve and compressed the time during that period. The scatter in values for the calcium values at higher concentrations is attributed to the electrode stability.

Figure 4 shows the effects of rinsing the acid washed coal with deionized water. It should be noted that the coal changes character in the process and the rate of passage of the deionized water decreased. Initially the acid was washed out of the column at pH 1.15. A period followed during which the pH changed from 1.15 to about 1.9 with a linear slope. The pH changed more rapidly and then asymptotically approached a value of about 3.3. The shape of the latter part of the curve approached that of a parabola. The initial linear portion is assumed to be due to the mixing of the acid in the space between the particles with the incoming water flow and discharge from the burette. The latter more parabolic shaped curve is believed to be due to diffusional processes from the pores of the particles.

One characteristic of the water washing step is the release of some calcium near the intersection of the linear and the non-linear parts of the pH curves. This is seen in Figure 4 and is reproducible through several stages of acid washing and water rinsing. The shape of the curve is consistent through 3 wash and rinse sequences. In each case the calcium is rinsed out near the intersection of the two segments of the pH versus time plots. The calcium is also washed out in successive acid washes in the same pH range.

The cause of the release of calcium in both the acid wash and water rinse near the same pH is not yet clear. It may be that the physical structure of form of the external surface changes at a certain pH. If that were so, then any calcium which had been freed from internal linkages to carboxylate or other groups might be released in the rearrangement step during the transition between the structures.

A small amount of cloudy material was seen in the supernatant water after the treated coal was removed from the burette. The cloudy material was decanted and allowed to settle. The clear supernatant was discarded. A grey solid was recovered and analyzed with FTIR.

FTIR indicated the presence of clay type minerals. Apparently the acid form of the coal is active and can release very finely divided clay material.

An analysis of the the acid solution which was passed over the coal in the burette for the experiment with the sodium electrode, and the rinse water, was made. The results are given in Table 1.

Table 1. Concentrations of Cationic Species in Wyodak Solutions in ppm (ug/ml)

Cation	Acid Soln	Rinse
Al	56.6	6.80
B	1.04	<.10
Ba	7.94	.37
Ca	908.	14.6
Fe	35.7	4.73
Mg	212.	1.26
Mn	1.21	.04
Ni	.21	<.05
Si	.55	<.30
Sr	16.5	.22
Ti	.07	.04
V	.13	<.10
Zn	.42	.05
K	4.91	<.20
Na	49.8	.19

The estimated accuracy of the ICP AES analysis is +/- 10%.

Be, Cd, Co, Cr, Cu, Mo, Pb, Sn, and Zr were all below the limits of determination.

The release of clay during the acid washing and subsequent water rinsing may indicate that the clay is attracted to negative groups such as the carboxylate in the coal structure. The clay has a number of cations bound in its layer structure. The rinse water following the acid wash contained some additional calcium, indicating the release of this cation during the duration of the contact with the water. It is possible that the coal structure includes coal-matter-to-clay bonds. Acid washing can rupture some of these linkages, permitting the liberation of the clay. The structure of the coal particle would then be weakened. This weakening would limit the useful life of low rank coals for uses such as ion exchange resins.

#### CONCLUSIONS:

1. some of the ion exchange properties of low rank coals can be understood by titrating with the burette system described.

2. Alkali cations are removed early in the titration, and alkaline earth cations are removed throughout the acid treatment.
3. More acid is consumed in the titration than the equivalent amount of cations which are recovered.
4. Some aluminum is solubilized.
5. Clay is released following the acid treatment. This clay is probably associated with the exchanged cations.

#### FUTURE WORK:

The potential of application of small amounts of catalysts which can still be useful needs to be explored. The ion exchange capabilities of the low rank coals presents an opportunity to add catalytically active species such as  $\text{Fe}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ . Other useful metal species, such as  $\text{MoO}_4^{-2}$ , can be added by adsorption techniques.

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FIGURE 1.  
DIAGRAM OF EQUIPMENT FOR ACID LEACHING OF COAL SAMPLES

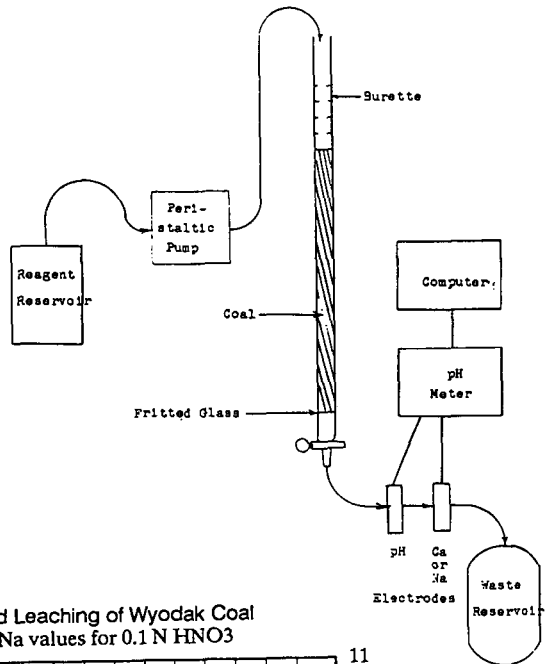
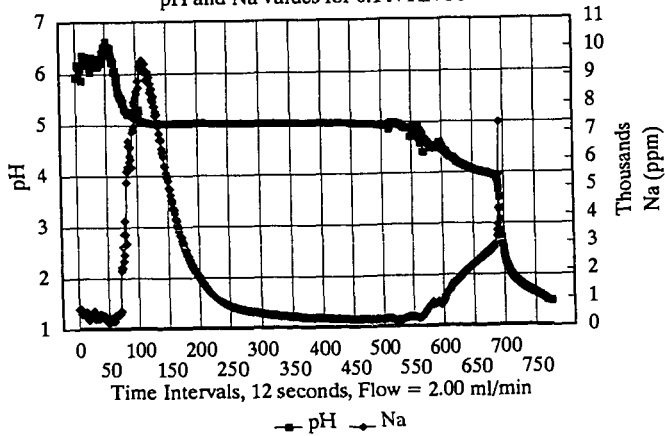
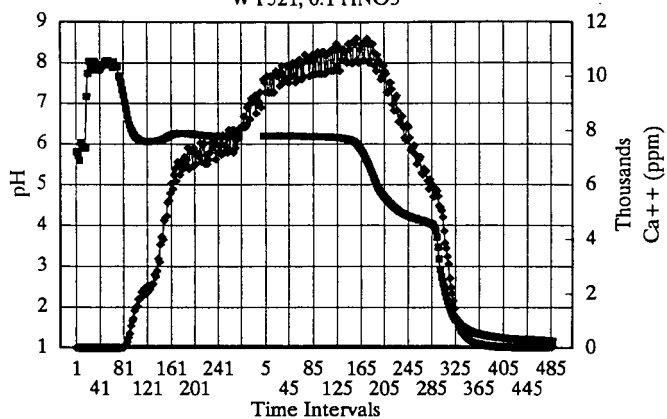


Fig. 2. Acid Leaching of Wyodak Coal  
pH and Na values for 0.1 N HNO<sub>3</sub>



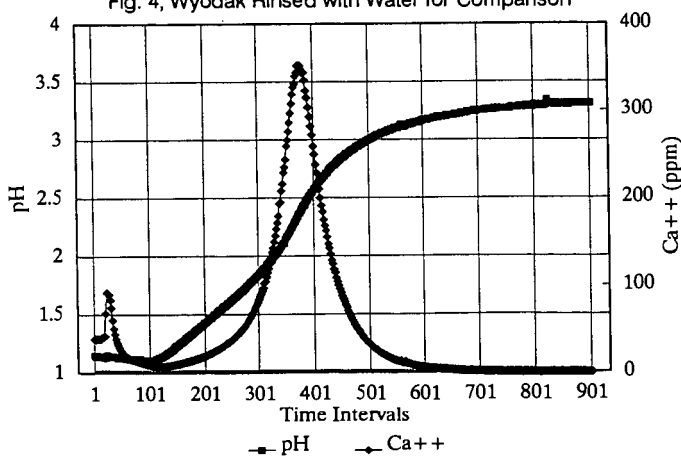
WY427S.wk3

Fig. 3, Wyodak Acid Washed for Comparison  
WY521, 0.1 HNO<sub>3</sub>



WY521 composite

Fig. 4, Wyodak Rinsed with Water for Comparison



WY521B